Theoretical and Experimental Studies of Regioselectivity in Selenoxide Elimination

Noboru Kondo, Hiroyuki Fueno, Hiroshi Fujimoto,* Mineyuki Makino, Hiroaki Nakaoka, Ikuo Aoki, and Sakae Uemura

Division of Molecular Engineering and Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan

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In order to gain insight into the mechanism of selenoxide elimination, the transition state structures have been determined by applying the ab initio MO method to the elimination for systems having a simplified skeleton, $CH_2(Y)CH(Se(O)CH_3)CH_3$ ($Y = OCH_3$, OH, CN and Cl). The calculations show that an allylic alkyl ether and an allylic alcohol should be produced preferentially in the case of $Y = OCH_3$ and OH, respectively, whereas a vinylic cyanide should be the major product in the case of Y = CN. The chloro-substituted model has given a result most consistent with the methoxy-substituted model. The elimination occurs via a transition state with a five-membered ring structure, and the breaking of the C_β–H bond takes place earlier than that of the Se–C_α bond, in the favorable path. The asynchronous nature of bond breaking is quite conspicuous in the cyano-substituted model, relative to the other systems. For comparison with the theoretical results, β-methoxy-, β-hydroxy-, β-cyano-, and β-chloro-substituted selenides were newly synthesized from *trans*-7-tetradecene, respectively, and were oxidized by H_2O_2 in tetrahydrofuran or in carbon tetrachloride. The regioselectivity observed for the elimination, i.e., the formation of a vinylic compound from the β-cyano selenide and a mixture of allylic and vinylic products from the β-chloro selenide, agrees well with the theoretical calculations. The difference in the activation energies of the two paths calculated for the model species is not large enough in the methoxy- and hydroxy-substituted selenides to explain the almost complete formation of an allylic compound in the physical experiments.

Introduction

Among the available methods for introducing an unsaturated carbon–carbon bond into organic molecules, the selenoxide elimination reaction has been shown to be quite useful because of its simple procedure and its characteristic regioselectivity. Jones, who first discovered the selenoxide elimination, proposed an intramolecular mechanism entailing a five-membered ring structure to explain its *syn* nature.[1,2] This proposition was shown to be correct by Sharpless who applied the method that was utilized by Cram to determine the stereochemistry in amine oxide elimination.[3,4] As for the orientation of elimination, the selenides with electron-withdrawing groups at β-positions (Y = OH, OR, OAc, $NHCOCH_3$, etc.) afford allylic compounds, whereas selenides with conjugative groups (Y = CN, COR, COOR, C=C, NO_2, SO_2R, etc.) yield vinylic compounds almost as the sole product (Scheme 1).[5-12] On the other hand, both allylic and vinylic compounds, in different ratios, are obtained from several other β-substituted selenides (Y = Cl, Br, NCS, N_3, $(CH_3)_2N$, etc.).[10,13]

Though numerous reports of selenoxide elimination have appeared, no reasonable explanation of the regioselectivity has been made. It is not clear, for example, whether or not the fission of the Se–C_α bond and that of the C_β–H bond take place in a concerted manner. The reaction has not been studied in detail from a theoretical perspective. As described in this report, we have examined the reaction mechanism of selenoxide elimination by locating the stable conformations of the selenoxides and the transition states of the elimination process on the potential energy surface. We have chosen models having a simplified selenoxide framework of $CH_2(Y)CH(Se(O)CH_3)CH_3$ with $Y = OCH_3$, OH, CN, and Cl. Population analysis has been used to understand the reactivity trend.[14] Experiments involving oxidative eliminations of β-substituted selenides of the same framework, bearing different Y groups [7-substituted 8-(phenylsele-

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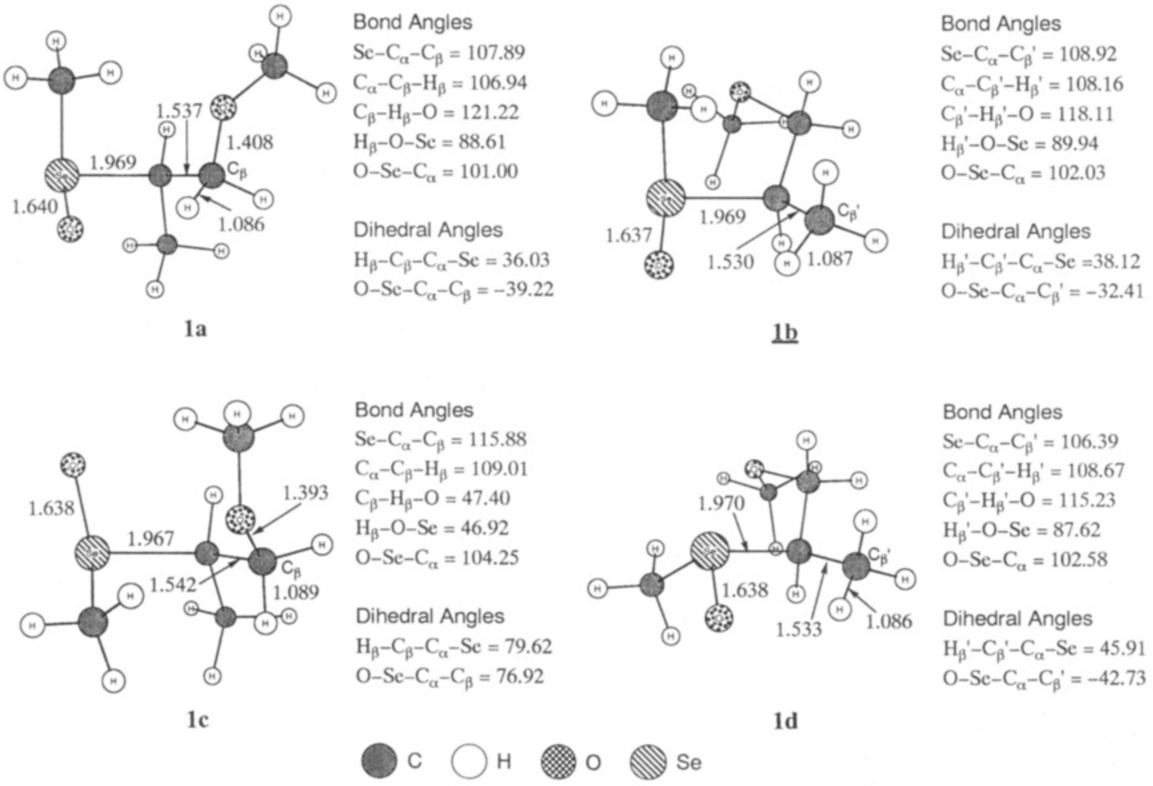

Bond Angles
$Se-C_\alpha-C_\beta = 107.89$
$C_\alpha-C_\beta-H_\beta = 106.94$
$C_\beta-H_\beta-O = 121.22$
$H_\beta-O-Se = 88.61$
$O-Se-C_\alpha = 101.00$

Dihedral Angles
$H_\beta-C_\beta-C_\alpha-Se = 36.03$
$O-Se-C_\alpha-C_\beta = -39.22$

1a

Bond Angles
$Se-C_\alpha-C_\beta' = 108.92$
$C_\alpha-C_\beta'-H_\beta' = 108.16$
$C_\beta'-H_\beta'-O = 118.11$
$H_\beta'-O-Se = 89.94$
$O-Se-C_\alpha = 102.03$

Dihedral Angles
$H_\beta'-C_\beta'-C_\alpha-Se = 38.12$
$O-Se-C_\alpha-C_\beta' = -32.41$

1b

Bond Angles
$Se-C_\alpha-C_\beta = 115.88$
$C_\alpha-C_\beta-H_\beta = 109.01$
$C_\beta-H_\beta-O = 47.40$
$H_\beta-O-Se = 46.92$
$O-Se-C_\alpha = 104.25$

Dihedral Angles
$H_\beta-C_\beta-C_\alpha-Se = 79.62$
$O-Se-C_\alpha-C_\beta = 76.92$

1c

Bond Angles
$Se-C_\alpha-C_\beta' = 106.39$
$C_\alpha-C_\beta'-H_\beta' = 108.67$
$C_\beta'-H_\beta'-O = 115.23$
$H_\beta'-O-Se = 87.62$
$O-Se-C_\alpha = 102.58$

Dihedral Angles
$H_\beta'-C_\beta'-C_\alpha-Se = 45.91$
$O-Se-C_\alpha-C_\beta' = -42.73$

1d

Figure 1. Calculated structures of $CH_2(OCH_3)CH(Se(O)CH_3)CH_3$.

no)tetradecanes] have also been carried out and the results compared with those of the theoretical studies.

Results and Discussion

Theoretical Calculations. Stable conformations of the selenoxide models and transition states for the elimination reaction were determined using the Gaussian 92 program.[15] A partially uncontracted split-valence basis set,[16] the STO-3G basis set or that with an effective core potential,[17] and the 3-21G(*) basis set[18] have often been utilized for the Se atom in the literature. The most practical set at present for the study of sizable organic systems seems to be the 3-21G basis set, augmented with polarization functions.[19-21] We adopted, for the present study, the 3-21G basis plus Huzinaga's d-type polarization functions for the Se atom and, to be consistent with this, for the C, N, O, and Cl atoms[22] and the 3-21G basis with the standard p-type polarization functions for the departing hydrogen atom.[22] The 3-21G basis was used for other hydrogens to conserve computing time. The systems treated were quite large, and therefore, the structures were determined at the restricted Hartree–Fock (RHF) level with the aid of vibration analysis using the analytical second derivatives of the total energy to see whether the calculated structure was at an energy minimum or at a saddle point. The calculated energies were corrected to include the electron correlation effect by the Møller–Plesset method to the second order (MP2//RHF).[23,24] Our primary purpose is to see the difference in the effects of substituent groups on the transition-state structures of selenoxide elimination.

We begin with a selenoxide model having the structural formula, $CH_2(OCH_3)CH(Se(O)CH_3)CH_3$, **1**. The four stable conformations **1a**–**1d** are illustrated in Figure 1. The system has many geometrical variables, and therefore, the present study covers a subset of possible conformations. For example, we have considered the paths yielding a vinylic product only with the *trans* configuration, since the carbon–carbon double bond in the product has one large group on each of the two carbon atoms in our reaction model. The calculated energies of the stable conformations **1a**–**1d** are presented in Table 1, together with those of the transition states, **TS1a**–**TS1d**.[25] Relative energy values are given in parentheses by taking **1b** as the reference. Among the four conforma-

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Scheme 1

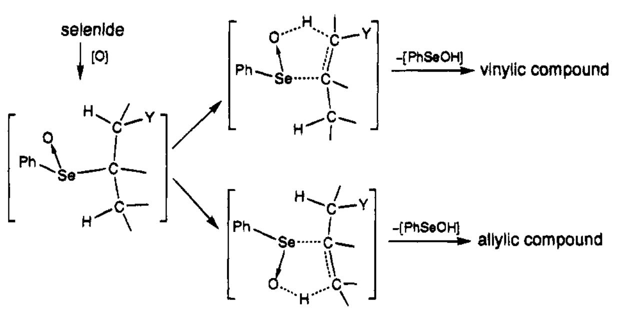


Table 1. Calculated Energies of Stable Structures and Transition States for Elimination from $CH_2(OCH_3)CH(Se(O)CH_3)CH_3$[a]

structures	RHF	MP2//RHF
1a	−2732.996 59 (0.23)	−2734.161 38 (0.41)
1b	−2732.996 99 (0.00)	−2734.162 06 (0.00)
1c	−2732.991 48 (3.12)	−2734.159 49 (1.74)
1d	−2732.994 72 (1.14)	−2734.157 20 (2.77)
TS1a	−2732.938 88 (32.81)	−2734.126 34 (18.76)
TS1b	−2732.945 72 (29.00)	−2734.130 96 (16.34)
TS1c	−2732.930 92 (37.53)	−2734.117 19 (24.22)
TS1d	−2732.942 76 (30.39)	−2734.126 32 (18.79)

[a] Total energy is in hartrees. Values in parentheses indicate the energy of the system in kcal/mol relative to **1b**, corrected for the zero-point vibration energy.[25]

tions of the selenoxide, **1b** is shown to have the lowest ground-state energy. The conformer **1a** is less stable than **1b** by only 0.23 kcal/mol at the RHF level and by 0.41 kcal/mol including the electron correlation effect.

We treat a selenoxide as the starting material and examine the reaction paths, some yielding an allylic compound and some giving a vinylic compound. The structures of the four transition states **TS1a-TS1d**, obtained for collapse of the selenoxide species, are illustrated in Figure 2. Here, the transition states **TS1a** and **TS1c** lead to a methyl 1-propenyl ether and **TS1b** and **TS1d** to an allylic methyl ether. All of these transition states have five-membered ring structures in which both the dihedral angle between the O—Se bond and the C_α—C_β bond (or the C_α—C_β' bond) around the Se—C_α bond axis and that between the Se—C_α bond and the C_β—H_β bond (or the C_β'—H_β' bond) around the C_α—C_β bond axis (or the C_α—C_β' bond axis) are smaller than 20°.

The transition state **TS1b** is of the lowest energy. The elimination reaction is most likely to take the path that starts from a selenide and goes through **TS1b** *via* the most stable conformation **1b** of the selenoxide to give an allylic ether as a product. The energy differences between **TS1b** and the other two transition states **TS1a** and **TS1d** are not so large, being ~2.4 kcal/mol at the MP2//RHF level of calculations. Thus, the path that connects **1d** and **TS1d** has almost the same barrier height as the path that connects **1b** and **TS1b**. One finds that this path leads to the same product, an allylic ether. The path that adopts the conformation **1a** of the selenoxide and **TS1a** to give a vinylic product is shown to have an activation barrier that is higher by only ~2 kcal/mol than the paths leading to an allylic ether. It is suggested then that an allylic ether should be the major product in this model system.

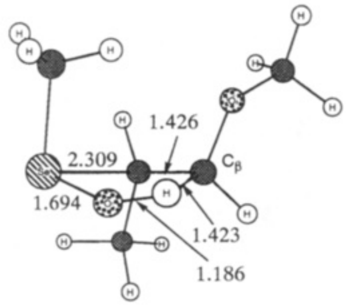
The preference for the alkoxy-substituted selenoxide, **1**, to give an allylic product is ascribed in part to the torsional effect. In **TS1c**, to give a vinylic product, both the methyl group on C_α and the methoxy group on C_β must be placed in positions that are nearly eclipsed with the hydrogens across the C_α—C_β bond. It is shown in Table 1 that **TS1c** is higher in energy than **TS1b** by ~8 kcal/mol. The larger H_β—C_β—C_α—Se dihedral angle in **TS1a** than in **TS1c** makes the eclipsing interactions weaker in the former. Such a repulsive interaction occurs only between the C_α—CH_2OCH_3 bond and a C_β'—H bond at the transition state **TS1b** or **TS1d**, to give an allylic product.

The elimination reaction of $CH_2(OH)CH(Se(O)CH_3)CH_3$, **2**, exhibits a trend similar to that of **1** both in structural changes and in energetics. The structures of **2** and the transition states for the elimination reaction are illustrated in Figures 3 and 4. The conformation **2a** is shown in Table 2 to be lower in energy than **2b** in this system. This conformation **2a**, as well as **2c**, appears to be stabilized by hydrogen bonding between the hydroxy group and the oxygen atom in the selenoxide skeleton. Thus, the activation barrier for the path going through **TS2a** (or **TS2c**) *via* **2a** (or **2c**) is considerably higher than that for **1**. If we assume, however, that the stabilization due to the hydrogen bonding is weakened by the interaction of the hydroxy group with the polar solvent molecules, e.g., tetrahydrofuran in physical experimental systems, the elimination reaction may take place *via* the conformer **2b** (or **2d**) in place of **2a** (or **2c**). The barrier height for the **2b** → **TS2b** path is ~16 kcal/mol, almost the same in magnitude as that for the lowest transition state for the decomposition of **1**. The path that goes through **TS2b** (or **TS2d**) affords an allylic alcohol as the major product of the elimination reaction. The relative energies of the transition states **TS2a**—**TS2d** are explained in a similar manner as in **1**, in terms of the torsional effects across the C_α—C_β (or C_α—C_β') bond.

We examine next a selenoxide model with a cyano group on one of the β carbons, $CH_2(CN)CH(Se(O)CH_3)CH_3$, **3**. Four conformations, **3a** and **3d** leading to a *trans*-vinylic product and **3b** and **3d** leading to an allylic product, have been considered for this species, as illustrated in Figure 5. The results summarized in Table 3 demonstrate that the conformation **3a** is most stable. The conformers **3b**, **3c**, and **3d** are less stable than **3a** by 2.9, 1.3, and 1.8 kcal/mol, respectively. The overlap repulsion between the methyl group on the Se atom and the cyanomethyl group on the C_α atom destabilizes the conformation **3b**.

The transition-state structures **TS3a-TS3d**, for the elimination reaction, are illustrated in Figure 6. Among the four transition states, **TS3a** leading to a 1-propenyl cyanide and **TS3c** leading to the same product are shown in Table 3 to have lower activation barriers than the transition states **TS3b** and **TS3d** that give rise to an allylic product. The energy difference between **TS3a** and **TS3d** is calculated to be 6.1 kcal/mol. The reaction should be selective in this system, yielding predominantly a vinylic cyanide.

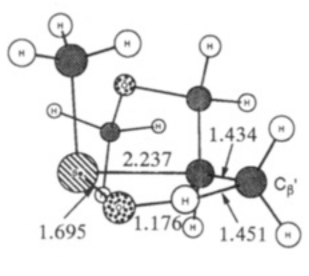
The changes in atomic populations and in overlap populations on going from the most stable conformation **1b** or **3a** to the lowest energy transition state **TS1b** or **TS3a** are illustrated in Figure 7 with respect to the β-methoxy-substituted and β-cyano-substituted selenoxide models.[14] Here, the signs + and − which follow the numbers indicate, respectively, an increase and a decrease in electron populations or in overlap populations. The calculations show that the electron population increases on C_β and decreases on C_α at the transition state. The Se—C_α bond is seen to be more polarized in



Bond Angles
$Se{-}C_\alpha{-}C_\beta = 98.68$
$C_\alpha{-}C_\beta{-}H_\beta = 97.20$
$C_\beta{-}H_\beta{-}O = 152.66$
$H_\beta{-}O{-}Se = 98.58$
$O{-}Se{-}C_\alpha = 88.03$

Dihedral Angles
$H_\beta{-}C_\beta{-}C_\alpha{-}Se = 17.64$
$O{-}Se{-}C_\alpha{-}C_\beta = -19.37$

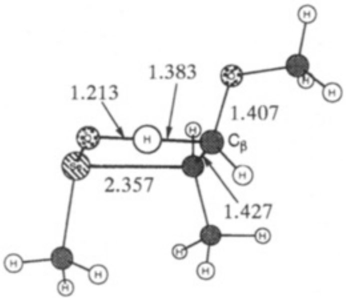
TS1a (1708.31*i* cm^{-1})



Bond Angles
$Se{-}C_\alpha{-}C_\beta' = 102.23$
$C_\alpha{-}C_\beta'{-}H_\beta' = 95.55$
$C_\beta'{-}H_\beta'{-}O = 152.48$
$H_\beta'{-}O{-}Se = 98.65$
$O{-}Se{-}C_\alpha = 88.78$

Dihedral Angles
$H_\beta'{-}C_\beta'{-}C_\alpha{-}Se = 10.78$
$O{-}Se{-}C_\alpha{-}C_\beta' = -14.70$

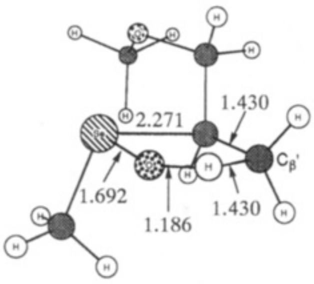
TS1b (1574.79*i* cm^{-1})



Bond Angles
$Se{-}C_\alpha{-}C_\beta = 99.10$
$C_\alpha{-}C_\beta{-}H_\beta = 98.47$
$C_\beta{-}H_\beta{-}O = 154.60$
$H_\beta{-}O{-}Se = 98.76$
$O{-}Se{-}C_\alpha = 87.76$

Dihedral Angles
$H_\beta{-}C_\beta{-}C_\alpha{-}Se = 4.09$
$O{-}Se{-}C_\alpha{-}C_\beta = -0.42$

TS1c (1755.29*i* cm^{-1})

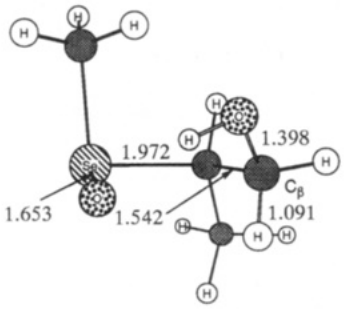


Bond Angles
$Se{-}C_\alpha{-}C_\beta' = 101.65$
$C_\alpha{-}C_\beta'{-}H_\beta' = 96.91$
$C_\beta'{-}H_\beta'{-}O = 153.37$
$H_\beta'{-}O{-}Se = 99.04$
$O{-}Se{-}C_\alpha = 88.96$

Dihedral Angles
$H_\beta'{-}C_\beta'{-}C_\alpha{-}Se = 1.77$
$O{-}Se{-}C_\alpha{-}C_\beta' = -1.40$

TS1d (1613.13*i* cm^{-1})

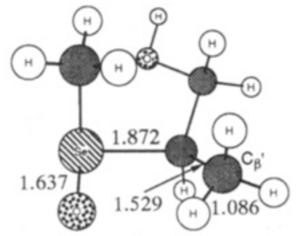
Figure 2. Transition-state structures for the elimination from $CH_2(OCH_3)CH(Se(O)CH_3)CH_3$.



Bond Angles
$Se{-}C_\alpha{-}C_\beta = 106.69$
$C_\alpha{-}C_\beta{-}H_\beta = 108.49$
$C_\beta{-}H_\beta{-}O = 84.62$
$H_\beta{-}O{-}Se = 86.89$
$O{-}Se{-}C_\alpha = 103.26$

Dihedral Angles
$H_\beta{-}C_\beta{-}C_\alpha{-}Se = 73.79$
$O{-}Se{-}C_\alpha{-}C_\beta = -13.86$

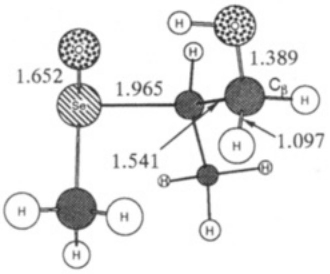
2a



Bond Angles
$Se{-}C_\alpha{-}C_\beta' = 108.85$
$C_\alpha{-}C_\beta'{-}H_\beta' = 108.33$
$C_\beta'{-}H_\beta'{-}O = 117.91$
$H_\beta'{-}O{-}Se = 90.63$
$O{-}Se{-}C_\alpha = 101.93$

Dihedral Angles
$H_\beta'{-}C_\beta'{-}C_\alpha{-}Se = 37.84$
$O{-}Se{-}C_\alpha{-}C_\beta' = -29.67$

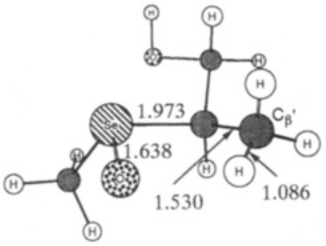
2b



Bond Angles
$Se{-}C_\alpha{-}C_\beta = 109.97$
$C_\alpha{-}C_\beta{-}H_\beta = 109.73$
$C_\beta{-}H_\beta{-}O = 72.42$
$H_\beta{-}O{-}Se = 71.53$
$O{-}Se{-}C_\alpha = 103.57$

Dihedral Angles
$H_\beta{-}C_\beta{-}C_\alpha{-}Se = 61.49$
$O{-}Se{-}C_\alpha{-}C_\beta = -31.72$

2c



Bond Angles
$Se{-}C_\alpha{-}C_\beta' = 107.56$
$C_\alpha{-}C_\beta'{-}H_\beta' = 108.49$
$C_\beta'{-}H_\beta'{-}O = 114.85$
$H_\beta'{-}O{-}Se = 89.14$
$O{-}Se{-}C_\alpha = 102.69$

Dihedral Angles
$H_\beta'{-}C_\beta'{-}C_\alpha{-}Se = 44.97$
$O{-}Se{-}C_\alpha{-}C_\beta' = -35.31$

2d

Figure 3. Calculated structures of $CH_2(OH)CH(Se(O)CH_3)CH_3$.

TS1b than in **TS3a**. The $C_\beta{-}H_\beta$ overlap population has been reduced to a greater extent in **TS3a** than in **TS1b**, whereas the decrease in the $Se{-}C_\alpha$ overlap population is much more significant in the latter.

Figure 6 indicates that the β-cyano group gets into position to have an effective conjugation with the $C_\alpha{-}C_\beta$ bond in **TS3a**. Naturally, the $C_\alpha{-}C_\beta$ bond is not as shortened as it is in the cases of β-methoxy- and β-hydroxy-substituted selenoxides. Vibration analysis demonstrates that the major structural change along the reaction coordinate is stretching of the $C_\beta{-}H_\beta$ (or $C_\beta'{-}H_\beta'$) bond at the transition states in the selenoxide elimination studied. Though the transition-state structures have been obtained at the restricted Hartree–Fock level, the present calculations seem to indicate an important aspect of the substituent effect. The lowest energy transition state **TS3a** for the β-cyano-substituted system has a shorter $Se{-}C_\alpha$ bond and a longer $C_\beta{-}H_\beta$ bond than the lowest energy transition state **TS1b** for the β-methoxy-substituted model and **TS2b** for the β-hydroxy-substi-

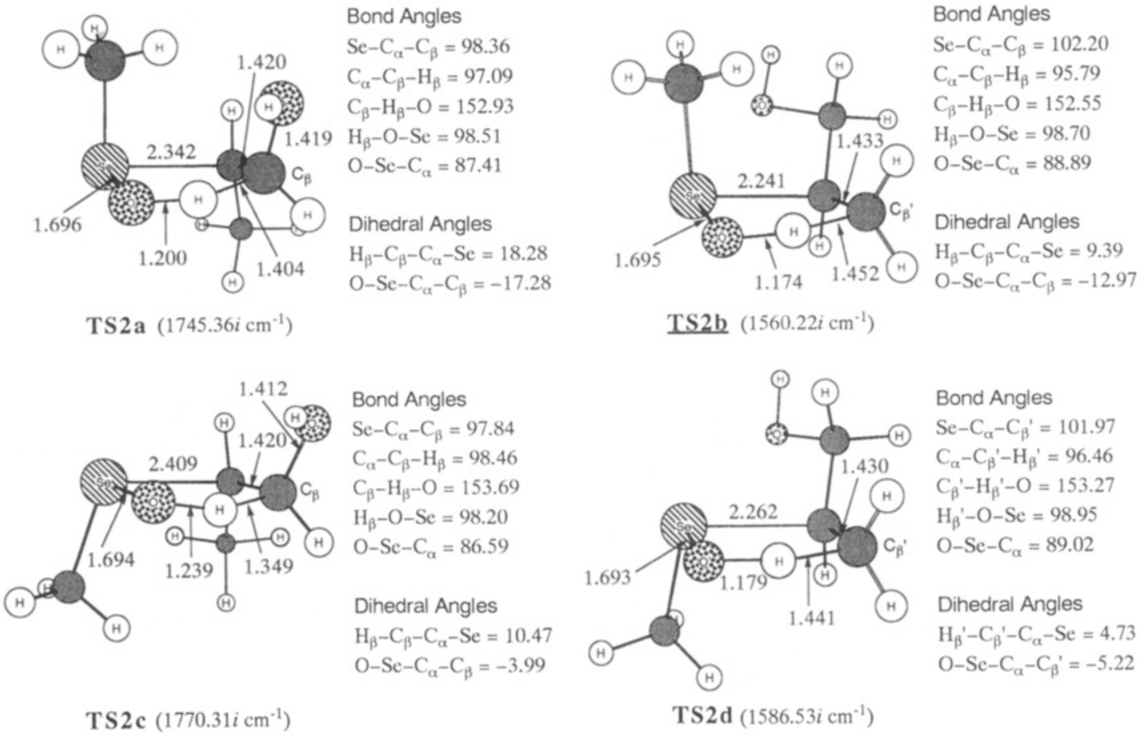


Figure 4. Transition-state structures for the elimination from $CH_2(OH)CH(Se(O)CH_3)CH_3$.

Table 2. Calculated Energies of Stable Structures and Transition States for Elimination from $CH_2(OH)CH(Se(O)CH_3)CH_3$[a]

structures	RHF	MP2//RHF
2a	−2694.164 33 (0.00)	−2695.198 32 (0.00)
2b	−2694.150 93 (7.61)	−2695.183 28 (8.64)
2c	−2694.160 15 (2.25)	−2695.192 16 (3.49)
2d	−2694.152 32 (6.65)	−2695.183 36 (8.50)
TS2a	−2694.094 01 (39.98)	−2695.149 75 (26.33)
TS2b	−2694.100 20 (36.28)	−2695.152 45 (24.82)
TS2c	−2694.087 35 (43.77)	−2695.141 21 (31.31)
TS2d	−2694.098 97 (36.68)	−2695.150 15 (25.90)

[a] Total energy is in hartrees. Values in parentheses indicate the energy of the system in kcal/mol relative to **2a**, corrected for the zero-point vibration energy.[25]

tuted model (C_β' and H_β' in place of C_β and H_β in these cases). The breaking of two bonds takes place in a concerted but less synchronized manner in the elimination reaction of **3** than in **1** or in **2**. The cyano group greatly stabilizes the anionic charge that develops on the β-carbon of **TS3a**.

It proved to be interesting to examine theoretically the effect of a chloro group on the selenoxide elimination. A mixture of an allylic compound and a vinylic compound was obtained as the product in experiments.[5b] The stable conformations of the β-chloro-substituted selenoxide model and the transition-state structures for the elimination reaction are presented in Figures 8 and 9. Among the four conformations of the selenoxide investigated here, the most stable is **4b** which leads to an allylic chloride upon elimination *via* the transition state **TS4b**. The barrier height has been calculated to be 15.7 kcal/mol at the MP2//RHF level of theory, as shown in Table 4. The transition state **TS4d** leading to the same product is slightly lower in energy than **TS4b**, but **TS4d** is derived from the conformation **4d** which has been located 0.61 kcal/mol above the most stable **4b**. The present calculation suggests that an allylic product is favored over a vinylic product, in this case.

The chloro substituent does not significantly stabilize the anionic charge that arises on C_β in the course of the elimination reaction, and the conjugation between the $C_\alpha-C_\beta$ bond and the substituent group is weaker than that in the β-cyano-substituted system, as indicated by the shorter $C_\alpha-C_\beta$ bond length in the chloro-substituted model. Then, the eclipsing interactions between the CH_3-C_α bond and the $C_\beta-H$ bond and between the $C_\beta-Cl$ bond and the $C_\alpha-H$ bond across the $C_\alpha-C_\beta$ bond make the transition state **TS4a** higher in energy than **TS4b** (or **TS4d**). The transition state **TS4a** is seen to have a longer $Se-C_\alpha$ distance than **TS3a** of the cyano-substituted model, indicating that two bonds have to be weakened in a more synchronous manner in **4** to give a vinylic product. In contrast, the transition states **TS4b** and **TS4d** that lead to an allylic product are favorable, having a longer $C_\beta'-H_\beta'$ bond and a shorter $Se-C_\alpha$ bond than the corresponding structures of the cyano-substituted model.

Experimental Results

As mentioned earlier, several elimination studies have been reported,[5-13] but the structures of the employed selenides and the oxidation conditions were not necessarily constant. In order to assess the explicit effect of β-substituents upon selenoxide elimination, for comparison with the results of MO calculations, we decided to carry out the oxidation of a series of selenides, differing only in the β-substituent, under a single set of conditions (Scheme 2). For this purpose, we synthesized the corresponding β-methoxy (**5**), β-hydroxy (**6**) β-cyano (**7**), and β-chloro selenides (**8**) from commercially available *trans*-7-tetradecene by reported methods or by a slightly modified method and used these as starting substrates.[9,12,13] These selenides were oxidized in tetrahydrofuran by excess 30% H_2O_2 at 0 °C except for **8**, which was too unstable to be isolated and so was oxidized *in situ* with excess 90% H_2O_2 in carbon tetrachloride, and

Table 3. Calculated Energies of Stable Structures and Transition States for Elimination from $CH_2(CN)CH(Se(O)CH_3)CH_3$[a]

structures	RHF	MP2//RHF
3a	−2710.960 97 (0.00)	−2712.087 09 (0.00)
3b	−2710.957 12 (2.47)	−2712.083 29 (2.92)
3c	−2710.959 00 (1.27)	−2712.085 86 (1.30)
3d	−2710.958 57 (1.45)	−2712.084 89 (1.81)
TS3a	−2710.923 96 (20.09)	−2712.065 67 (10.80)
TS3b	−2710.902 17 (33.75)	−2712.050 49 (20.31)
TS3c	−2710.919 78 (22.78)	−2712.060 82 (13.91)
TS3d	−2710.907 62 (30.15)	−2712.055 58 (16.94)

[a] Total energy is in hartrees. Values in parentheses indicate the energy of the system in kcal/mol relative to **3a**, corrected for the zero-point vibration energy.[25]

the elimination products were identified and characterized. From β-methoxy selenide, only the corresponding *trans*-allylic methyl ether **9** was produced, its *cis*-isomer and the corresponding methyl vinyl ether not being observed. In the case of the β-hydroxy selenide, the corresponding *trans*-allylic alcohol (**10**) was produced in high yield together with a small amount of α,β-unsaturated ketone (**12**), while the formation of a vinylic alcohol (saturated ketone) was not detected at all. The compound **12** was identified by GC−MS directly and also by comparison of its retention time with that of the product prepared by oxidation of the compound **10** with MnO_2. Its formation was observed at an early stage of the oxidation, suggesting that the ketone was not derived from the initially produced alcohol, though the mechanism of its formation is not certain. In the case of β-cyano selenide, only the corresponding vinylic cyanide (**11**) was produced in high yield, the formation of the corresponding allylic cyanide not being detected. In the case of β-chloro selenide on the other hand, the formation of a mixture of the corresponding allylic chloride (**13**) and vinylic chloride (**14**) (80:20, 83% isolated yield based on the starting 7-tetradecene) was observed by GLC and ^1H-NMR. It has been reported that oxidation of various 2-chloroalkyl phenyl selenides gives a mixture of the corresponding allylic chlorides and vinylic chlorides, its ratio greatly depending on the structure of the starting selenides.[5b,10b,13] Although the stereochemistry of **11** and **14** was not confirmed unambiguously, *trans*-addition of a PhSeY species[5b,12] followed by *syn*-selenoxide elimination might produce them stereospecifically.

The difference in barrier heights between the path leading to an allylic product and that leading to a vinylic product, calculated above for the β-methoxy- and β-hydroxy-substituted selenoxide models, does not appear to be large enough relative to the cyano-substituted and chloro-substituted models, but the results of the present theoretical study are in line with the experimental results, for the most part.

Conclusion

Our calculations have shown that selenoxide elimination takes place *via* a transition state having a five-membered cyclic structure. The model species $CH_2(OCH_3)CH(Se(O)CH_3)CH_3$ has been shown to have the transition state with the lowest activation barrier that leads to an allylic methyl ether. The barrier height has been found to be ~16 kcal/mol, a transition state leading to a vinylic compound being located 2.4 kcal/mol above. The species $CH_2(OH)CH(Se(O)CH_3)CH_3$ shows similar features. On the other hand, the species $CH_2(CN)CH(Se(O)CH_3)CH_3$ opts for the path that leads to a vinylic product rather than the one that leads to an allylic product and has a larger difference in the barrier heights and a lower activation energy than the elimination reaction of the methoxy- or hydroxy-substituted species. The calculation on the chloro-substituted species has given a result that is more consistent with the methoxy- or

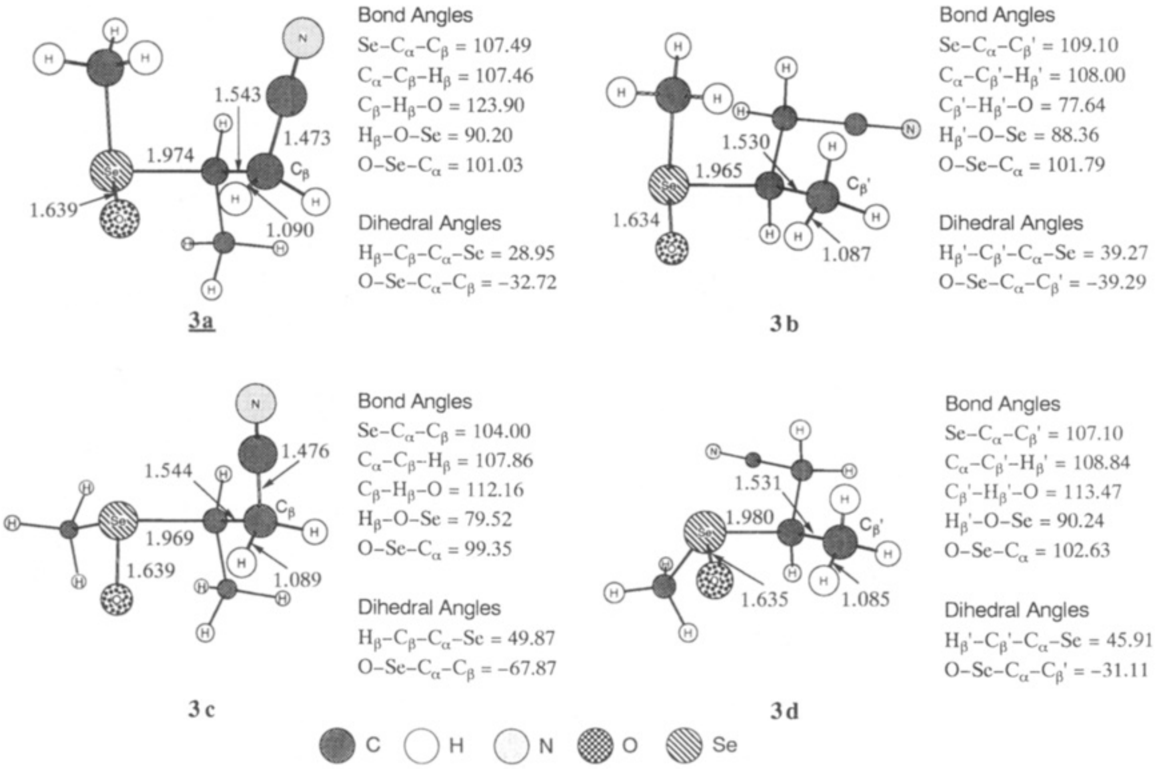
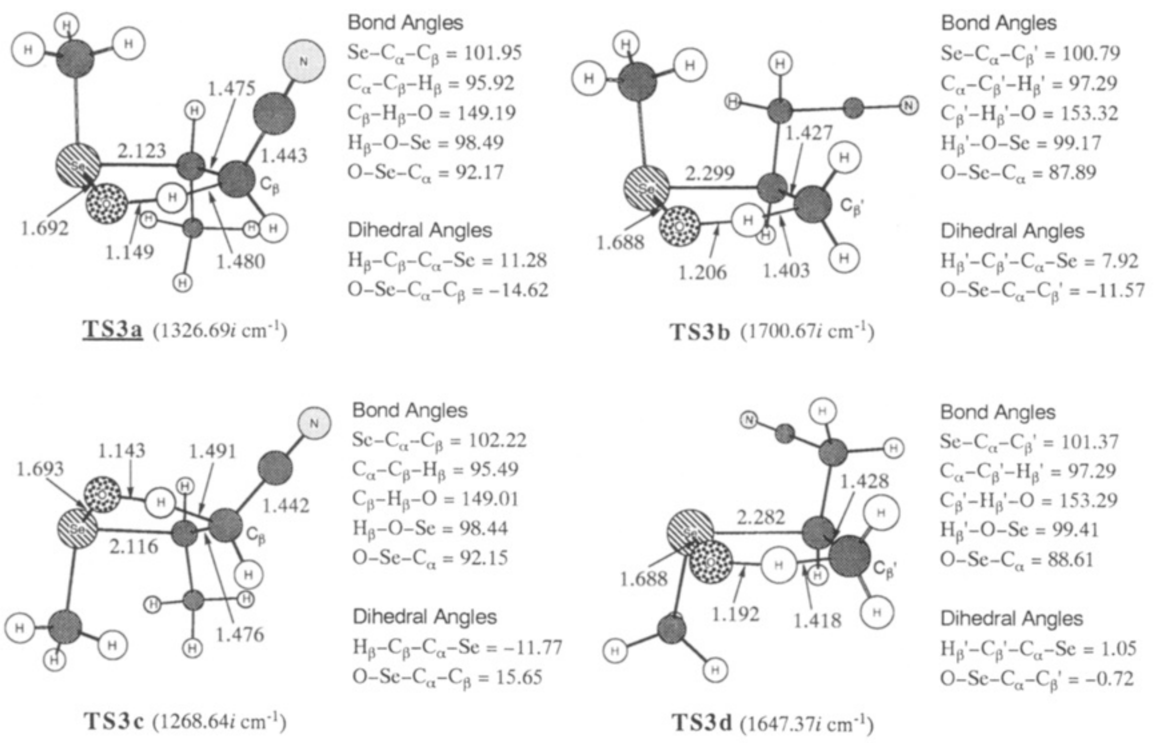


Figure 5. Calculated structures of $CH_2(CN)CH(Se(O)CH_3)CH_3$.



Bond Angles
$Se-C_\alpha-C_\beta = 101.95$
$C_\alpha-C_\beta-H_\beta = 95.92$
$C_\beta-H_\beta-O = 149.19$
$H_\beta-O-Se = 98.49$
$O-Se-C_\alpha = 92.17$

Dihedral Angles
$H_\beta-C_\beta-C_\alpha-Se = 11.28$
$O-Se-C_\alpha-C_\beta = -14.62$

TS3a (1326.69i cm^{-1})

Bond Angles
$Se-C_\alpha-C_\beta' = 100.79$
$C_\alpha-C_\beta'-H_\beta' = 97.29$
$C_\beta'-H_\beta'-O = 153.32$
$H_\beta'-O-Se = 99.17$
$O-Se-C_\alpha = 87.89$

Dihedral Angles
$H_\beta'-C_\beta'-C_\alpha-Se = 7.92$
$O-Se-C_\alpha-C_\beta' = -11.57$

TS3b (1700.67i cm^{-1})

Bond Angles
$Se-C_\alpha-C_\beta = 102.22$
$C_\alpha-C_\beta-H_\beta = 95.49$
$C_\beta-H_\beta-O = 149.01$
$H_\beta-O-Se = 98.44$
$O-Se-C_\alpha = 92.15$

Dihedral Angles
$H_\beta-C_\beta-C_\alpha-Se = -11.77$
$O-Se-C_\alpha-C_\beta = 15.65$

TS3c (1268.64i cm^{-1})

Bond Angles
$Se-C_\alpha-C_\beta' = 101.37$
$C_\alpha-C_\beta'-H_\beta' = 97.29$
$C_\beta'-H_\beta'-O = 153.29$
$H_\beta'-O-Se = 99.41$
$O-Se-C_\alpha = 88.61$

Dihedral Angles
$H_\beta'-C_\beta'-C_\alpha-Se = 1.05$
$O-Se-C_\alpha-C_\beta' = -0.72$

TS3d (1647.37i cm^{-1})

Figure 6. Transition-state structures for the elimination from $CH_2(CN)CH(Se(O)CH_3)CH_3$.

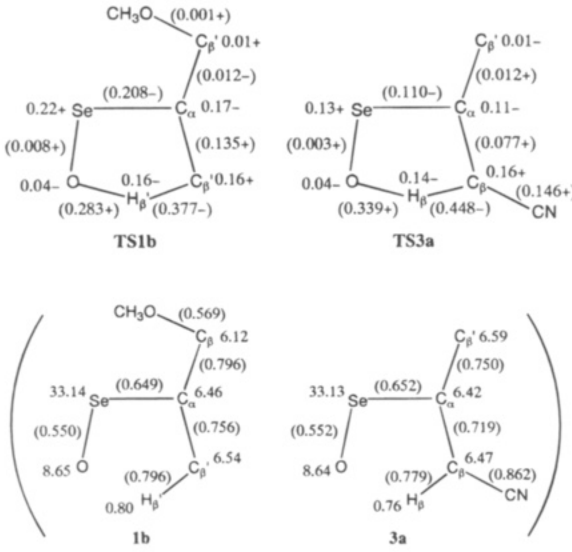


Figure 7. Changes in atomic populations (without parentheses) and in overlap populations (in parentheses) on going from the most stable conformation to the lowest energy transition state in $CH_2(OCH_3)CH(Se(O)CH_3)CH_3$ and in $CH_2(CN)CH(Se(O)CH_3)CH_3$. The signs + and − placed behind numbers indicate an increase and a decrease in populations, respectively. Atomic and overlap populations of **1b** and **3a** are shown for the reference.

hydroxy-substituted species. It is suggested that the energy difference between the two paths, calculated for the methoxy- or hydroxy-substituted cases, has to be somewhat larger to support the results of the physical experiments. It is not clear at present whether this relatively small energy difference should be ascribed to the accuracy of the calculations[26] or whether some other factors that are not involved in our model calculations are operating.

The substituent group seems to control the regioselectivity of the selenoxide elimination by affecting the concerted cleavage of the $Se-C_\alpha$ and $C_\beta-H_\beta$ bonds. The breaking of the $C_\beta-H_\beta$ bond has been found to take place earlier than that of the $Se-C_\alpha$ bond in the favorable paths in the collapse of all of the selenoxide models studied above. The negative charge that arises on C_β in the course of the elimination reaction is stabilized through conjugation by a cyano group attached to that carbon. Thus, the asynchronous nature of the bond breaking is more conspicuous in the β-cyano-substituted system than in the other systems. The experimental results obtained for the elimination of selenoxides derived from *trans*-7-tetradecene show reasonable agreement with the theoretical results.

Experimental Section

General Procedures. ^1H (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were measured with a JEOL GSX-270 spectrometer using TMS as an internal standard in $CDCl_3$. Chemical shifts are reported in δ units downfield from TMS. Mass spectra were obtained on a Shimadzu QP-2000 spectrometer. GLC analyses were carried out with a Shimadzu GC-14A with flame ionization detectors equipped with a CBP10-S25-050 column (Shimadzu, fused silica capillary column, 0.33 mm × 25 m, 0.5-μm film thickness) using nitrogen as carrier gas. GLC yields were determined using suitable hydrocarbons as internal standards. The isolation of pure products was carried out with column chromatography (Wakogel C-200, 100-200

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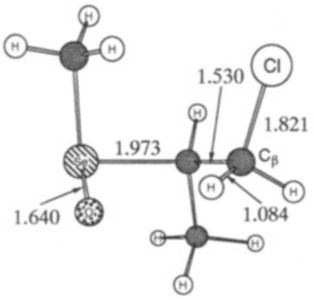
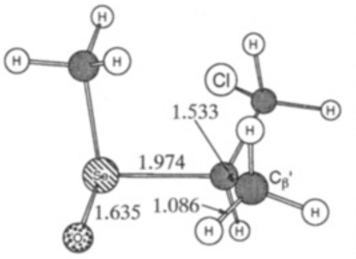
(26) The geometry optimization of **TS1b** and **TS3a** at the MP2/3-21G* level of theory gave the following results. **TS1b**: bond lengths (Å) $Se-C_\alpha$ 2.296, $C_\alpha-C_{\beta'}$ 1.420, $C_{\beta'}-H_{\beta'}$ 1.422, $H_{\beta'}-O$ 1.192, and Se−O 1.721, bond angles (deg) $Se-C_\alpha-C_{\beta'}$ 101.30, $C_\alpha-C_{\beta'}-H_{\beta'}$ 96.16, $C_{\beta'}-H_{\beta'}-O$ 154.50, $H_{\beta'}-O-Se$ 97.91, and $O-Se-C_\alpha$ 87.18, dihedral angles (deg) $H_{\beta'}-C_{\beta'}-C_\alpha-Se$ 12.61, and $O-Se-C_\alpha-C_{\beta'}$ 10.57. **TS3a**: bond lengths (Å) $Se-C_\alpha$ 2.225, $C_\alpha-C_\beta$ 1.442, $C_\beta-H_\beta$ 1.444, $H_\beta-O$ 1.167, and Se−O 1.715, bond angles (deg) $Se-C_\alpha-C_\beta$ 101.00, $C_\alpha-C_\beta-H_\beta$ 97.26, $C_\beta-H_\beta-O$ 152.18, $H_\beta-O-Se$ 98.01, and $O-Se-C_\alpha$ 89.78, dihedral angles (deg) $H_\beta-C_\beta-C_\alpha-Se$ 10.20 and $O-Se-C_\alpha-C_\beta$ 12.74. The $Se-C_\alpha$ bond in this calculation is considerably longer than that determined disregarding the electron correlation effect both in **TS1b** and in **TS3a**. It is seen that **TS3a** has a longer $Se-C_\alpha$ bond and a shorter $C_\beta-H_\beta$ bond than **TS1b**, in line with the results of calculation at the RHF level.



Bond Angles
$Se-C_\alpha-C_\beta = 108.18$
$C_\alpha-C_\beta-H_\beta = 109.22$
$C_\beta-H_\beta-O = 122.28$
$H_\beta-O-Se = 89.62$
$O-Se-C_\alpha = 100.95$

Dihedral Angles
$H_\beta-C_\beta-C_\alpha-Se = 26.11$
$O-Se-C_\alpha-C_\beta = -33.56$

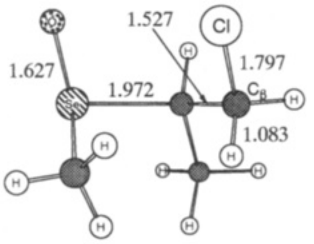
4a



Bond Angles
$Se-C_\alpha-C_\beta' = 108.45$
$C_\alpha-C_\beta'-H_\beta' = 108.08$
$C_\beta'-H_\beta'-O = 118.77$
$H_\beta'-O-Se = 90.72$
$O-Se-C_\alpha = 101.44$

Dihedral Angles
$H_\beta'-C_\beta'-C_\alpha-Se = 37.48$
$O-Se-C_\alpha-C_\beta' = -31.81$

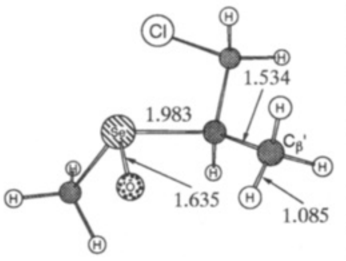
4b



Bond Angles
$Se-C_\alpha-C_\beta = 116.58$
$C_\alpha-C_\beta-H_\beta = 112.07$
$C_\beta-H_\beta-O = 57.91$
$H_\beta-O-Se = 51.30$
$O-Se-C_\alpha = 106.94$

Dihedral Angles
$H_\beta-C_\beta-C_\alpha-Se = 112.07$
$O-Se-C_\alpha-C_\beta = 69.36$

4c

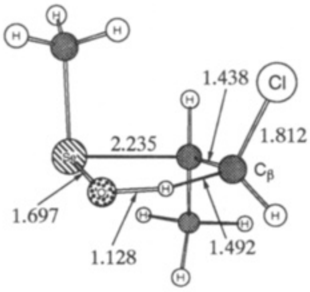


Bond Angles
$Se-C_\alpha-C_\beta' = 107.24$
$C_\alpha-C_\beta'-H_\beta' = 108.83$
$C'_\beta-H_\beta'-O = 113.05$
$H_\beta'-O-Se = 90.89$
$O-Se-C_\alpha = 102.83$

Dihedral Angles
$H_\beta'-C_\beta'-C_\alpha-Se = 44.30$
$O-Se-C_\alpha-C_\beta' = -24.63$

4d

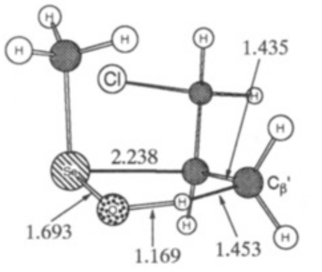
Figure 8. Calculated structures of $CH_2(Cl)CH(Se(O)CH_3)CH_3$.



Bond Angles
$Se-C_\alpha-C_\beta = 100.46$
$C_\alpha-C_\beta-H_\beta = 97.52$
$C_\beta-H_\beta-O = 150.72$
$H_\beta-O-Se = 99.47$
$O-Se-C_\alpha = 90.08$

Dihedral Angles
$H_\beta-C_\beta-C_\alpha-Se = 10.53$
$O-Se-C_\alpha-C_\beta = -12.49$

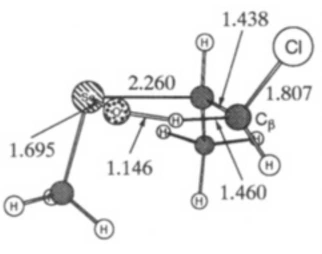
TS4a (1260.08*i* cm^{-1})



Bond Angles
$Se-C_\alpha-C_\beta' = 102.08$
$C_\alpha-C_\beta'-H_\beta' = 95.74$
$C_\beta'-H_\beta'-O = 152.17$
$H_\beta'-O-Se = 99.07$
$O-Se-C_\alpha = 88.65$

Dihedral Angles
$H_\beta'-C_\beta'-C_\alpha-Se = 10.56$
$O-Se-C_\alpha-C_\beta' = -14.54$

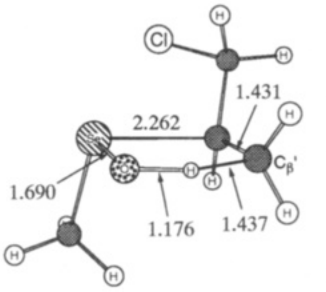
TS4b (1549.29*i* cm^{-1})



Bond Angles
$Se-C_\alpha-C_\beta = 100.13$
$C_\alpha-C_\beta-H_\beta = 98.32$
$C_\beta-H_\beta-O = 151.71$
$H_\beta-O-Se = 99.14$
$O-Se-C_\alpha = 89.79$

Dihedral Angles
$H_\beta-C_\beta-C_\alpha-Se = -2.33$
$O-Se-C_\alpha-C_\beta = 6.05$

TS4c (1407.23*i* cm^{-1})



Bond Angles
$Se-C_\alpha-C_\beta' = 101.87$
$C_\alpha-C_\beta'-H_\beta' = 96.68$
$C_\beta'-H_\beta'-O = 152.98$
$H_\beta'-O-Se = 99.37$
$O-Se-C_\alpha = 88.91$

Dihedral Angles
$H_\beta'-C_\beta'-C_\alpha-Se = 3.44$
$O-Se-C_\alpha-C_\beta' = 2.40$

TS4d (1583.10*i* cm^{-1})

Figure 9. Transition-state structures for the elimination from $CH_2(Cl)CH(Se(O)CH_3)CH_3$.

mesh) and with medium-pressure column chromatography (Merck silica gel 60, 230-400 mesh).

Commercially available compounds were used without further purification except for the solvent, which was distilled by standard methods before use.

7-Methoxy-8-(phenylseleno)tetradecane (5). The compound was prepared by slightly modifying the literature methods.[5b,9a] To a solution of phenylselenenyl bromide (0.370 g, 1.57 mmol), prepared from diphenyl diselenide and bromine, in CH_3OH (15 mL) at room temperature were slowly added *trans*-7-tetradecene (0.334 g, 1.70 mmol) in CH_3OH (5 mL) and then anhydrous copper(I) sulfate (0.070 g, 0.437 mmol), and the resulting solution was stirred at 45 °C for 12 h. After the solution had been cooled to room temperature, it was poured into saturated NaCl (aq) (40 mL), extracted with diethyl ether (30 mL × 3), and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure left a yellow liquid which was subjected to medium-pressure column chromatography (3% ethyl acetate−hexane as eluent) to give **5** (0.578 g, 89% yield) in a pure form: ^1H NMR ($CDCl_3$) δ 0.84-0.90 (6H, m), 1.24-1.65 (20H, m), 3.25−3.33 (2H, C*H*Se and C*H*OCH_3, m), 3.35 (3H, s), 7.24−7.27 (3H, m), 7.56−7.60 (2H, m); ^{13}C NMR ($CDCl_3$) δ 22.56 (q), 25.79 (t), 28.25 (t), 29.07 (t), 29.31 (t), 31.45 (t), 31.64 (t), 31.77 (t), 50.95 (d), 57.89 (q), 84.15 (d), 127.08 (d), 128.80

Table 4. Calculated Energies of Stable Structures and Transition States for Elimination of $CH_2(Cl)CH(Se(O)CH_3)CH_3$[a]

structures	RHF	MP2//RHF
4a	−3076.461 19 (0.05)	−3077.453 80 (0.60)
4b	−3076.461 22 (0.00)	−3077.454 87 (0.00)
4c	−3076.450 13 (6.72)	−3077.443 51 (6.89)
4d	−3076.461 09 (0.06)	−3077.453 68 (0.61)
TS4a	−3076.412 29 (27.18)	−3077.421 35 (17.51)
TS4b	−3076.410 13 (28.85)	−3077.424 66 (15.74)
TS4c	−3076.407 19 (30.41)	−3077.416 75 (20.43)
TS4d	−3076.410 85 (28.21)	−3077.424 79 (15.47)

[a] Total energy is in hartrees. Values in parentheses indicate the energy of the system in kcal/mol relative to **4b**, corrected for the zero-point vibration energy.[25]

(d), 130.63 (s), 134.52 (d). Anal. Calcd for $C_{21}H_{36}OSe$: C, 65.77; H, 9.46. Found: C, 65.96; H, 9.61.

8-(Phenylseleno)-7-tetradecanol (6). The compound was prepared by treatment of *trans*-7-tetradecene (1.04 g, 5.32 mmol) with phenylselenenyl chloride (1.21 g, 6.11 mmol) in CH_3CN−water (5:1) (18 mL) at room temperature for 24 h according to a literature method,[9d] and the product **6** was isolated by column chromatography (SiO_2; 10% ethyl acetate−hexane as eluent) as a yellow liquid (1.47 g, 75% yield) in a pure form: ^1H NMR ($CDCl_3$) δ 0.84−0.89 (6H, m), 1.25−1.75 (20H, m), 2.32 (1H, d, J = 5.8 Hz, O*H*), 3.29 (1H, dt, J = 9.3 and 3.3 Hz, C*H*Se), 3.62 (1H, m, C*H*OH), 7.22−7.28 (3H, m), 7.54−7.59 (2H, m); ^{13}C NMR ($CDCl_3$) δ 14.00 (q), 22.52 (t), 26.12 (t), 28.39 (t), 29.02 (t), 29.16 (t), 30.24 (t), 31.60 (t), 31.69 (t), 33.60 (t), 56.35 (d), 72.82 (d), 127.41 (d), 129.02 (d), 129.53 (s), 134.37 (d). Anal. Calcd for $C_{20}H_{34}OSe$: C, 65.02; H, 9.28. Found: C, 65.05; H, 9.05.

7-Cyano-8-(phenylseleno)tetradecane (7). The compound was prepared by treatment of *trans*-7-tetradecene (0.385 g, 1.97 mmol) and phenylselenocyanate[12a] (0.421 g, 2.13 mmol) in the presence of tin(IV) chloride (1.28 g, 4.77 mmol) in CH_2Cl_2 (8 mL) at room temperature for 48 h, according to a literature method,[12b] and the product was isolated by column chromatography (SiO_2; 10% ethyl acetate−hexane as eluent) as a yellow liquid (0.559 g, 75% yield) in a pure form: ^1H NMR ($CDCl_3$) δ 0.84−0.91 (6H, m), 1.21−1.86 (20H, m), 2.74 (1H, C*H*CN, dt, J = 9.7 and 4.7 Hz), 3.09 (1H, C*H*Se, dt, J = 9.7 and 4.8 Hz), 7.25−7.35 (3H, m), 7.56−7.60 (2H, m); ^{13}C NMR ($CDCl_3$) δ 13.88 (q), 13.94 (q), 22.37 (t), 22.46 (t), 27.03 (t), 27.86 (t), 28.43 (t), 28.77 (t), 30.90 (t), 31.32 (t), 31.51 (t), 32.17 (t) 38.51 (d), 46.45 (d), 120.45 (s; CN), 128.17 (d), 128.17 (s?), 129.18 (d), 135.34 (d). Anal. Calcd for $C_{21}H_{33}NSe$: C, 66.65; H, 8.79; N, 3.70. Found: C, 66.88; H, 8.69; N, 3.41.

Selenoxide Elimination of 5−7 with 30% H_2O_2. To a solution of **6** (0.167 g, 0.453 mmol) in THF (1 mL) at 0 °C was added 30% H_2O_2 (0.4 mL, 4.2 mmol) portion by portion, and the resulting solution was stirred at 0 °C for 0.5 h and then at room temperature for 1.5 h. It was poured into saturated NaCl (aq) (30 mL), extracted with diethyl ether (20 mL × 3), and dried over $MgSO_4$. GLC analysis showed the presence of **10** and a small amount of **12** (total yield 78%). For isolation, five times scale reaction was carried out, and a mixture of **10** and **12** was isolated as a pale yellow liquid (60%) by column chromatography (SiO_2; 10% ethyl acetate−hexane as eluent). The compound **12** was prepared separately by treatment of **10** with MnO_2 in hexane at room temperature for 1 h (97% isolated yield).

8-Tetradecen-7-ol (10): ^1H NMR ($CDCl_3$) δ 0.86−0.91 (6H, m), 1.28−1.54 (17H, m), 2.02 (2H, q, J = 6.8 Hz), 4.03 (1H, C*H*OH, q, J = 6.6 Hz), 5.44 (1H, =C*H*CH(OH), ddt, J = 15.4, 6.6 and 1.2 Hz), 5.63 (1H, =C*H*CH$_2$, dt, J = 15.4 and 6.8 Hz); MS *m/z* (relative intensity) 212 (M$^+$, 0.2), 194 (1.5), 169 (0.6), 155 (2.3), 141 (7.6), 127 (27.3), 109 (24.0), 95 (5.1), 81 (12.9), 67 (32.5), 57 (100.0), 43 (48.4).

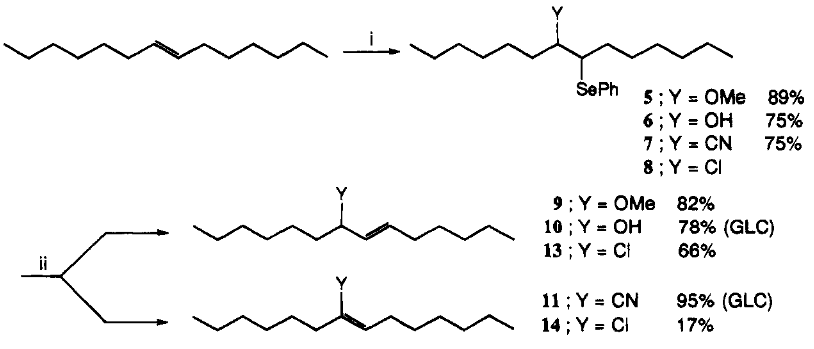
8-Tetradecen-7-one (12): ^1H NMR ($CDCl_3$) δ 0.86−0.89 (6H, m), 1.28−1.59 (14H, m), 2.17 (2H, =CC*H*$_2$, dq, J = 6.9 and 1.6 Hz), 2.49 (2H, C*H*$_2$CO, t, J = 7.4 Hz), 6.07 (1H, =C*H*CO, dt, J = 15.9 and 1.6 Hz), 6.80 (1H, =C*H*CH$_2$, dt, J = 15.9 and 6.9 Hz); MS *m/z* (relative intensity) 210 (M$^+$, 0.3), 181 (0.5), 167 (1.0), 153 (1.0), 139 (13.0), 125 (22.1), 111 (3.8), 97 (12.2), 82 (8.4), 70 (22.6), 55 (100.0), 41 (36.0).

The oxidation of β-methoxy (**5**) and β-cyano selenide (**7**) was similarly carried out and each product was isolated by the method described above.

7-Methoxy-8-tetradecene (9): a pale yellow liquid, 82% isolated yield; ^1H NMR ($CDCl_3$) δ 0.85-0.91 (6H, m), 1.27−1.64 (16H, m), 2.05 (2H, q, J = 6.7 Hz), 3.24 (3H, s), 3.44 (1H, C*H*OCH$_3$, q, J = 8.2 Hz), 5.23 (1H, =C*H*CH(OCH$_3$), ddt, J = 15.4, 8.2 and 1.4 Hz), 5.59 (1H, =C*H*CH$_2$, dt, J = 15.4 and 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.08 (q), 22.50 (t), 22.61 (t), 25.41 (t), 28.97 (t), 29.28 (t), 31.35 (t), 31.85 (t), 32.20 (t), 35.65 (t), 55.72 (q), 82.71 (d), 130.55 (d), 134.31 (d); MS *m/z* (relative intensity) 226 (M$^+$, 0.2), 155 (3.4), 141 (66.7), 109 (10.6), 95 (4.0), 81 (9.2), 71 (100.0), 67 (26.0), 55 (24.3), 41 (49.9). Anal. Calcd for $C_{15}H_{30}O$: C, 79.57; H, 13.36. Found: C, 79.28; H, 13.33.

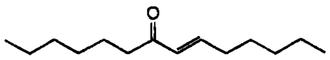
2-Hexyl-2-nonenenitrile (11): a pale yellow liquid, 75% isolated yield; ^1H NMR ($CDCl_3$) δ 0.86−0.91 (6H, m), 1.27−1.58 (16H, m), 2.19 (2H, C*H*$_2$C(CN)=, td, J = 7.4 and 1.2 Hz), 2.34 (2H, =CHC*H*$_2$, q, J = 7.4 Hz), 6.12 (1H, =C*H*, tt, J = 7.4 and 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.00 (q), 22.51 (t), 28.01 (t), 28.26 (t), 28.61 (t), 28.69 (t), 31.42 (t), 31.47 (t), 31.51 (t), 34.19

Scheme 2



(i) Y = OMe; PhSeCl / MeOH / $CuSO_4$ / 45°C, 12h. Y = OH; PhSeCl / MeOH-H_2O / rt, 24h. Y = CN; PhSeCN / $SnCl_4$ / CH_2Cl_2 / rt, 48h. Y = Cl; PhSeCl / CCl_4 / 0°C, 1.5h

(ii) 9~10eq. 30% or 90% H_2O_2 / THF or CCl_4 / 0°C, 0.5h then rt, 1.5h.



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(t), 114.68 (s, =*C*(CN)), 117.83 (s, *C*N), 147.69 (d, *C*H=); MS *m/z* (relative intensity) 221 (M^+, 0.5), 220 (1.2), 207 (3.2), 206 (3.3), 192 (5.5), 178 (5.2), 164 (9.0), 150 (20.6), 138 (16.2), 120 (12.5), 108 (19.6), 97 (31.0), 83 (25.2), 69 (42.4), 55 (42.9), 43 (100.0).

Preparation of 7-Chloro-8-(phenylseleno)tetradecane (8) and Its Selenoxide Elimination Giving the Compounds 13 and 14. The compound **8** was prepared *in situ* by treatment of *trans*-7-tetradecene (0.397 g, 2.02 mmol) with phenylselenenyl chloride (0.472 g, 2.46 mmol) in CCl_4 (10 mL) at room temperature for 1.5 h with stirring.[5b,13] To the resulting solution was added 90% H_2O_2 (0.7 mL, 18.5 mmol) portion by portion at 0 °C during 0.5 h, and then the solution was stirred at room temperature for 1.5 h. It was poured into saturated Na_2CO_3 (aq) (100 mL) and extracted with CH_2Cl_2 (50 mL × 3). The extract was washed with saturated NaCl (aq) (100 mL) and dried over $MgSO_4$. GLC analysis showed the presence of two products in a ca. 4:1 ratio. Evaporation of the solvent left a pale yellow oil which was distilled (Kugelrohr, 100−120 °C/2 Torr) to afford a mixture of 1-hexyl-2-octenyl chloride (**13**) and 1-hexyl-1-octenyl chloride (**14**) as a colorless liquid (0.388 g, 1.68 mmol, 83% yield based on the starting 7-tetradecene) in a pure form. ^{1}H-NMR analysis revealed the ratio of **13** and **14** to be 80:20. **13**: ^{1}H NMR ($CDCl_3$) δ 0.80−0.90 (6H, m), 1.20−1.60 (14H, m), 1.72−1.90 (2H, m), 2.01−2.10 (2H, m), 4.33 (1H, C*H*Cl, dt, $J = 8.90$ and 7.26 Hz), 5.50 (1H, =C*H*CH(Cl), $J = 15.18$ and 8.90 Hz), 5.67 (1H, =C*H*CH$_2$, dt, $J = 15.18$ and 6.60 Hz); ^{13}C NMR ($CDCl_3$) δ 63.86 (d, *C*Cl), 131.05 (d, *C*H=CHC(Cl)), 133.62 (d, =*C*HC(Cl)); other signals mainly ascribable to **13**, 14.05 (q), 22.50 (t), 22.57 (t), 26.61 (t), 28.62 (t), 28.71 (t), 31.34 (t), 31.70 (t), 31.92 (t), 39.17 (t); MS *m/z* (relative intensity) 232 ($M^+ + 2$, 1.5), 230 (M^+, 5.5), 194 (1.5), 123 (4.2), 109 (10.5), 95 (20.8), 82 (54.8), 69 (54.6), 55 (65.7), 43 (100.0). **14**: ^{1}H NMR ($CDCl_3$) δ 0.80−0.90 (6H, m), 1.20−1.60 (16H, m), 2.15 (2H, m), 2.29 (2H, C*H*$_2$C(Cl)=, t, $J = 7.26$ Hz), 5.42 (1H, =C*H*CH$_2$, t, $J = 8.25$ Hz); ^{13}C NMR ($CDCl_3$) δ 125.42 (d, =*C*H), 134.68 (s, =*C*Cl); MS *m/z* (relative intensity) 194 (11.1), 110 (10.2), 95 (30.7), 81 (65.9), 67 (100.0), 54 (38.9), 41 (58.1). Anal. Calcd for $C_{14}H_{27}Cl$: C, 72.85; H, 11.79. Found (as a mixture of **13** and **14**): C, 73.27; H, 12.13.

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