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REVIEW

Selectivity in Selenoxide and Telluroxide Eliminations as Double Bond Forming Reactions*

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Some aspects of the oxidation of organic selenides and tellurides leading to selenoxide and telluroxide eliminations to form a double bond have been reviewed as follows: (i) the rate of oxidation of selenides to selenoxides in comparison with that of sulfides to sulfoxides, (ii) the stereochemistry of eliminations, (iii) the reactivity order of sulfoxide, selenoxide, and telluroxide eliminations, (iv) the effect of a substituent on the rate of elimination, (v) the effect of β-substituents (Y) in an alkyl group upon the regioselectivity of the selenoxide elimination, (vi) new aspects of the telluroxide elimination. As to (v), an allylic compound [$\rangle$C=C—C(Y)—] was almost the sole product when Y=OH, OR, OAc, and $NHCOCH_3$, while a vinylic compound [$\rangle$C=C(Y)—C—] was the main or the sole product when Y=CN, COR, CO_2R, C=C, C≡C, NCS, NO_2, and SO_2 (the substituents which can be conjugated with a double bond). The regioselectivity is still obscure when $Y=N_3$, NR_2, halogen, and S, because of the lack of the data to be discussed.

KEY WORDS: Selenoxide elimination/ Telluroxide elimination/ Olefin formation/ Organic selenides/ Organic tellurides/

1. Introduction

The selenoxide elimination has been utilized in organic synthesis as one of the best methods for introducing a carbon-carbon double bond into organic molecules. Some excellent reviews on organoselenium chemistry are available which cover the wide area of this subject[1~3]. Until quite recently, on the other hand, the telluroxide elimination has not been recognized as a good tool for the formation of double bonds.[4] In this article we describe some aspects of the chemistry of the selenoxide and telluroxide eliminations, especially focusing on the effect of β-substituents in an alkyl group upon the regioselectivity of the selenoxide elimination and also on recent development of the

* This review article was accepted on the occasion of the retirement of Professor Emeritus Masaya Okano and is dedicated to him.

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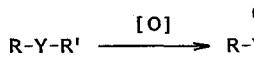
telluroxide elimination.

2. The Rate of Oxidation

The selenoxide elimination usually occurs *in situ* by oxidation of alkyl aryl selenide with a suitable oxidizing agent. The rate of oxidation of selenides to selenoxides has been examined using ozone in an inert solvent (CCl_4, $CHCl_3$, CH_3NO_2) at −10−−50°C (Scheme 1).[5] Dialkyl selenides are oxidized more rapidly than diaryl selenides.



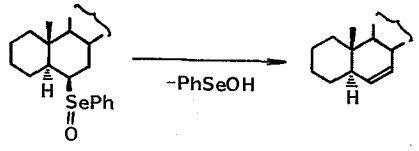
Scheme 1

Relative rate: Bu_2Se, 34; BuSePh, 4; Ph_2Se, 1;
$Me_2C{=}CHEt$, <1; Bu_2S, ≪1

Although dialkyl sulfides are oxidized some 50 times less rapidly than do olefins, selenides are oxidized more rapidly than olefins. This difference in the oxidation rate is utilized in the selective conversion of alkenyl phenyl selenides to the corresponding selenoxides using various oxidizing agents[6~10] and also in the selective oxidation of selenide in the presence of sulfide using hydrogen peroxide.[11] When sodium periodate ($NaIO_4$) or *meta*-chloroperbenzoic acid (m-CPBA) was used, selenides were converted to selenoxides without affecting the aldehyde functional group of the same molecule.[12,13] To our knowledge, no data are available for the rate of oxidation of tellurides to telluroxides in comparison with those of selenides and sulfides.

3. The Stereochemistry of Elimination

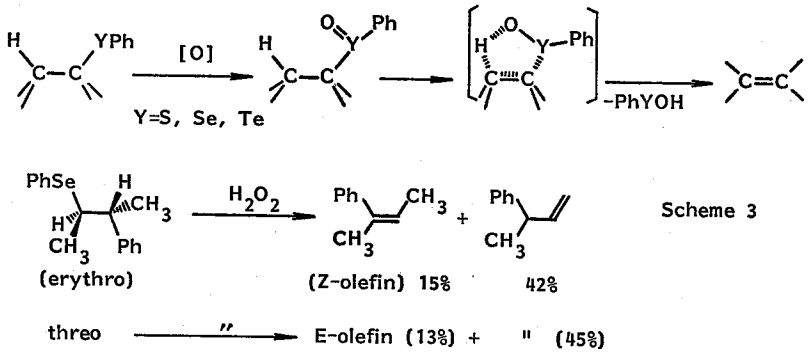
The *syn*-nature of the selenoxide elimination was suggested by Jones *et al.*[14] on the basis of the fact that 6β-phenylseleninyl-5α-cholestane decomposed to afford 5α-cholest-6-ene as a sole steroidal product (and no cholest-5-ene) (Scheme 2).



(S), (R)

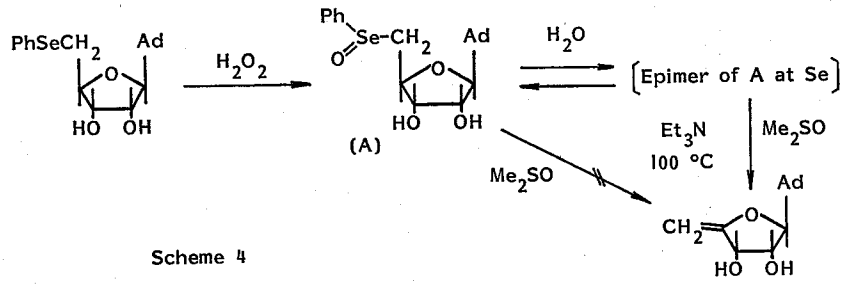
Scheme 2

The different rate of decomposition between two diastereomeric selenides [(S) and (R)] (diastereomer at Se) was attributed to a cyclic intramolecular mechanism usually associated with *syn*-eliminations.[14,15] The stereochemisty of the selenoxide elimination was proven unambiguously by Sharpless *et al.*[16] to be *syn* by applying the sequence used by Cram[17] for determining the stereochemistry of the elimination of amine oxide. Thus, the oxidation of *erythro*-selenide afforded only Z-olefin, and that of *threo*-selenide gave only E-olefin (Scheme 3). The related sulfoxide elimination has also been shown to be *syn*[18]. The different rate of the selenoxide elimination in the diastereomeric



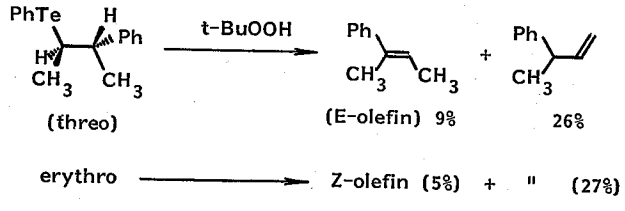
Scheme 3

selenoxides described above was also observed in the synthesis of 4′, 5′-unsaturated nucleosides[19]. One diastereoisomer (A) of the selenoxides afforded a mixture of several unidentified products when heated in anhydrous dimethyl sulfoxide (Me_2SO). However, when (A) was allowed to epimerize in the presence of water, the desired unsaturated nucleoside was obtained in a yield of 94% (Scheme 4). The tellurides



Scheme 4

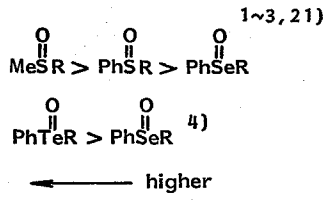
analogous to the selenides shown in Scheme 3 were oxidized with *tert*-butylhydroperoxide (t-BuOOH) to afford olefins, although in somewhat insufficient yields, stereo-selectively and -specifically (Scheme 5)[20]. Thus, the stereochemistry of the telluroxide elimination seems also to be *syn* as in the cases of the related sulfoxide and selenoxide eliminations.



Scheme 5

4. The Reactivity Order of Eliminations

The temperature required for the elimination reaction lies in the order shown in Scheme 6[1~4,21]. This means that both sulfoxide and telluroxide eliminations need a higher temperature than that required for the selenoxide elimination. Some physical



Scheme 6

cf. pK: Me_2SOH^+, 0; Me_2SeOH^+, 2.55; Me_2TeOH^+, ~6

D.M.: Ph_2SO, 4.08, Ph_2SeO, 4.44; $(p\text{-}CH_3C_6H_4)_2TeO$, 3.93

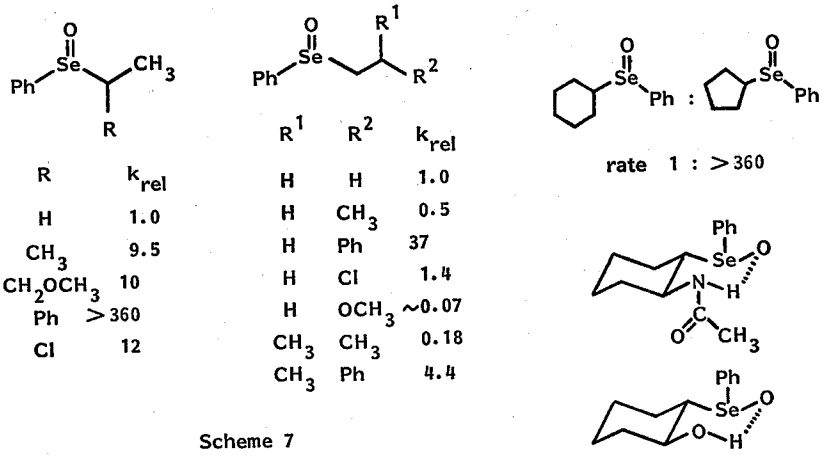
constants such as the dissociation constant and the dipole moment which may be related to this order are also listed in Scheme 6. The dissociation constant of the protonated sulfoxide, selenoxide, and telluroxide[22] may reflect the affinity of oxygen atom with β-hydrogen which eliminates, but the listed values can not explain why a higher temperature is required for the telluroxide elimination. The dipole moment[23] may reflect the polarity of a chalcogen-oxygen bond, and it seems reasonable to assume that the elimination reaction proceeds more rapidly as the dipole moment becomes larger. Kwart *et al.*[24] compared the deuterium isotope effect in the selenoxide elimination reaction with that of the sulfoxide elimination and concluded that the ease of the selenoxide elimination or, namely, the lowering of the activation energy for the elimination can be attributed to a severe shortening of the distance between the oxygen and carbon centers involved in a hydrogen transfer.

5. The Effect of a Substituent on the Rate of Elimination

When the selenoxide elimination is used in a synthetic procedure, alkyl aryl selenides (or sometimes methyl alkyl selenides) are generally used as starting compounds in order to introduce a double bond into the alkyl group unambiguously. By the introduction of a substituent into either aryl or alkyl group, the rate of elimination is influenced.

5.1 The Effect of a Substituent on an Alkyl Group

The effect of a substituent on an alkyl group was studied by comparing the rate of elimination of ethyl phenyl selenoxide bearing various substituents on the α and β position of ethyl group in $CDCl_3$ at 38°C containing 1.5 equivalent of Me_2NH.[25] Relative rates are summarized in Scheme 7. The rate of elimination was increased by the introduction of a substituent into the α position of ethyl group, irrespective of the electron-donating or -withdrawing nature of the substituent. The large effect of a phenyl group may be attributed to the resonance effect of the phenyl group with the double bond produced. The introduction of a methyl group into the β position of an ethyl group slightly decreased the rate of elimination as compared to the statistical value (2/3). A methoxy group on the β position decreased the rate extremely, while a chlorine atom on the β position increased the rate slightly. The selenoxide elimination of cyclopentyl phenyl selenoxide is unusually fast, whereas that of cyclohexyl phenyl selenoxide is unusually slow.[25] This anomalous results were attributed to the favorable and unfavorable dihedral angle between carbon-selenium and carbon-

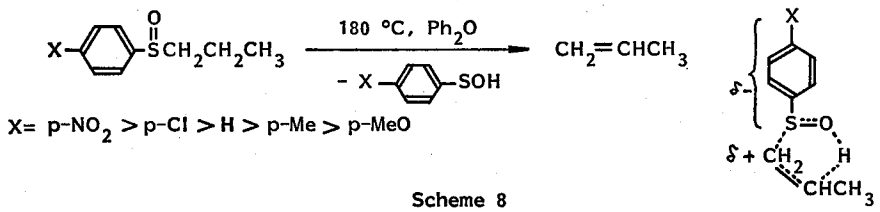


Scheme 7

hydrogen bonds for the selenoxide elimination. Anomalous stability of β-acetamido-[26,27] and β-hydroxy-cyclohexyl[28,29] phenyl selenoxides has been reported and the stability was attributed to an intramolecular hydrogen bond as shown in Scheme 7 on the basis of IR and NMR spectra.

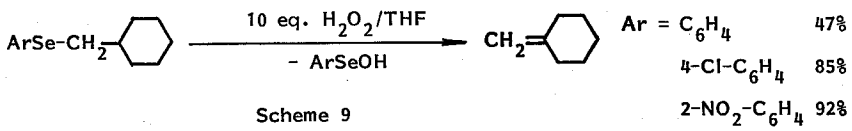
5.2 The Effect of a Substituent on an Aryl Group

Emerson *et al.*[30] have studied the rate of pyrolysis of *para*-substituted phenyl propyl sulfides in diphenyl ether as solvent and found that the electron-withdrawing substituents increased the rate of olefin formation in the order shown in Scheme 8.

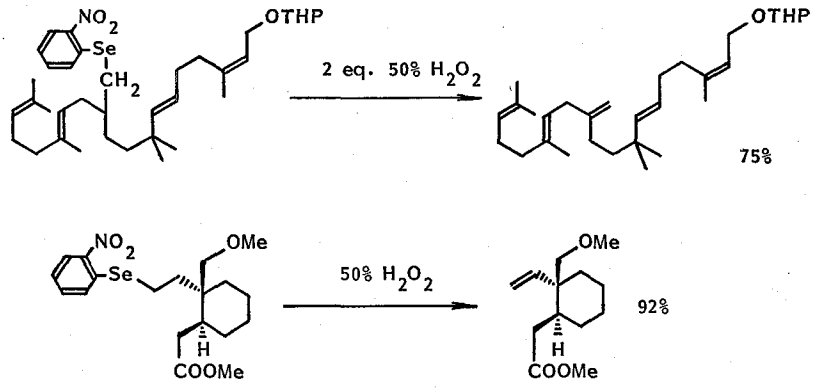


Scheme 8

These data were correlated by a Hammett plot giving $\rho = +0.51$. The most reasonable transition state of this reaction was depicted in Scheme 8 on the basis of these data and the enthalpy and entropy of activation of the reaction. This observation was utilized in olefin synthesis *via* the selenoxide elimination. Sharpless *et al.*[31] reported that in certain cases the yields of olefins were incerased dramatically by the introduction of an electron-withdrawing substituent into 2- or 4-position of an aromatic ring. Typical results are summarized in Scheme 9. Elegant applications of this finding were the formation of a double bond in one step of the total synthesis of natural products such

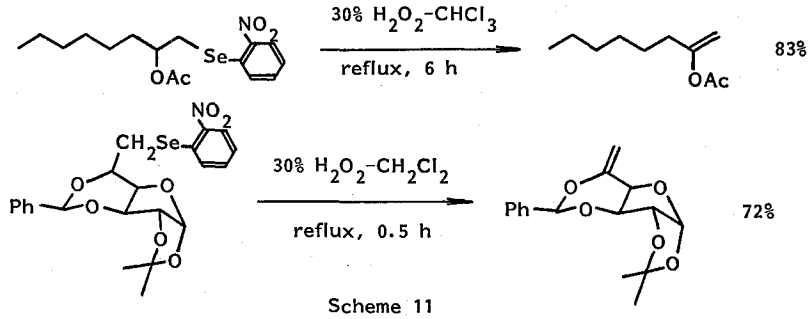


Scheme 9



Scheme 10

as moenocinol[32] and vernolepin[33] (Scheme 10). In the latter case (a model compound) it was noted that the yield of olefin was disappointingly low when a phenylseleno analogue was used instead of 2-nitrophenylseleno compound. In the case where the oxidative elimination of phenyl selenide did not proceed due to the presence of an oxygen functional group at β position of alkyl group or the expected elimination products can not tollerate under severe reaction conditions because of their instability, satisfactory results were sometimes obtained by the oxidative elimination of the corresponding 2-nitrophenyl selenides[34] (Scheme 11). Schmidt *et al.*[35] adopted the

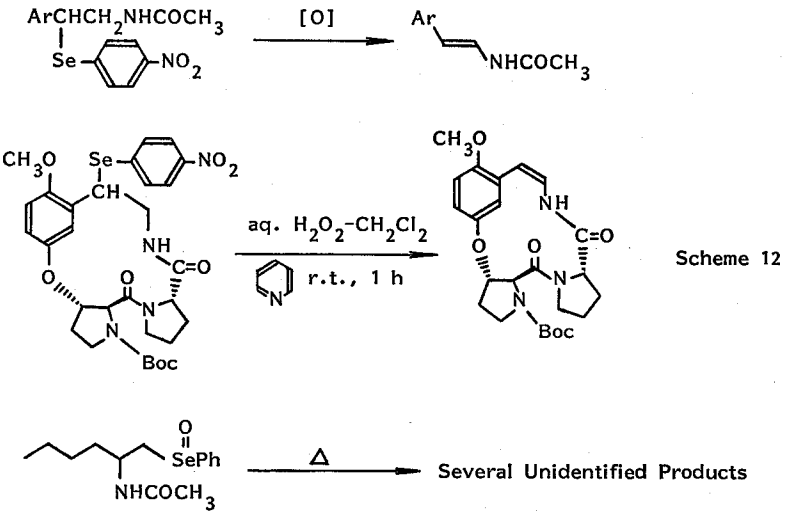


Scheme 11

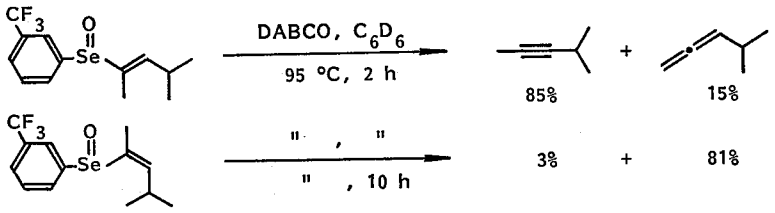
selenoxide elimination reaction of 4-nitrophenyl selenide for the synthesis of enamide, and utilized the reaction in the total synthesis of peptide alkaloid of a biologically active natural ansa compound, zizyphine A (Scheme 12). Although E olefin was introduced into a linear compund, Z compound of lower energy was produced in the oxidative elimination of cyclic ansa amide. We have observed[36] that the pyrolysis of β-acetamidohexyl phenyl selenoxide, prepared by amidoselenation[27,37] of 1-hexene, afforded unworkable mixture of products.

The rate constants for the elimination of a substituted phenyl ethyl selenoxide were measured and the results were correlated by a Hammett plot giving $\rho=+0.8$.[25]

The formation of acetylenes and/or allenes by *syn* elimination of vinyl selenoxides was reported.[10] In the presence of 1, 4-diazabicyclo[2.2.2]octane (DABCO), *meta*-trifluoromethylphenyl vinyl selenoxides afforded mainly acetylenes when *cis*-



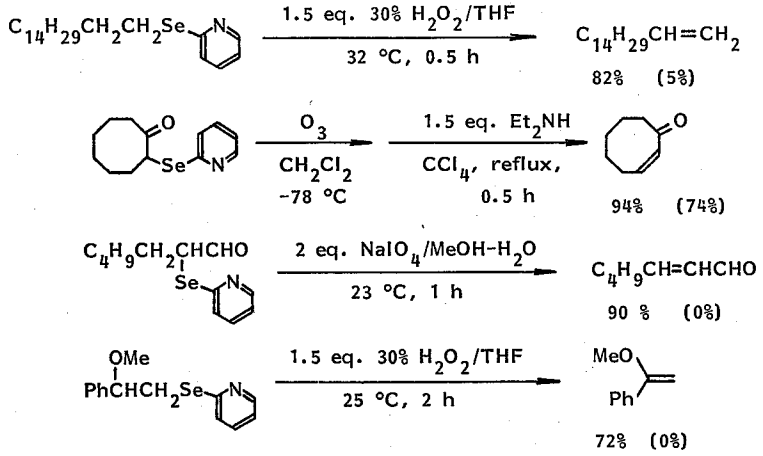
Scheme 12



Scheme 13

hydrogen is available, while allenes were the main products when *cis*-hydrogen is not available (Scheme 13).

Pyridine is another good candidate of an electron defficient aromatic ring. In fact, it has been reported that the oxidative elimination of alkyl 2-pyridyl selenides affords olefins in good yields even in the cases where satisfactory results are not obtained



Scheme 14

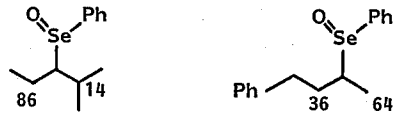
by oxidation of the corresponding phenyl selenides. As summarized in Scheme 14, the formations of terminal olefins,[38] α,β-unsaturated carbonyl compounds,[39] and enol ethers[40] are good examples of this reaction. The yields in parenthesis are those obtained from phenyl analogues under the same conditions.

6. The Regioselectivity of the Selenoxide Elimination

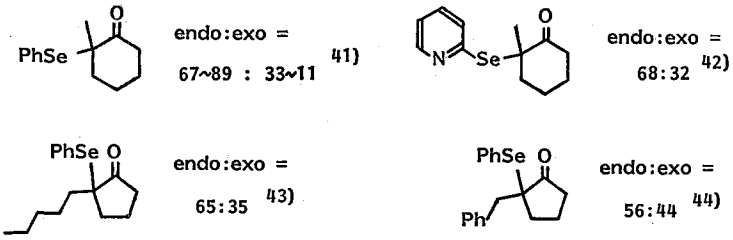
When a hydrogen atom for elimination is available from both adjacent carbon atoms, it is possible that the selenoxide elimination proceeds in two directions to afford regioisomeric mixtures of olefins. Here, substituents of β position of an alkyl group play the most important role in determining the direction of elimination. This section is divided to subsections according to the nature of the atom of a substituent on β position.

6.1 Carbon Substituent

Although the selenoxide elimination shows a preference for elimination toward the less substituted carbon, the selectivity is not so high as to be used in synthetic reactions (Scheme 15)[8,16]. In the cases of α-alkyl α-arylseleno cycloalkanones, however, the formation of *endo*-olefin (elimination toward more substituted carbon)

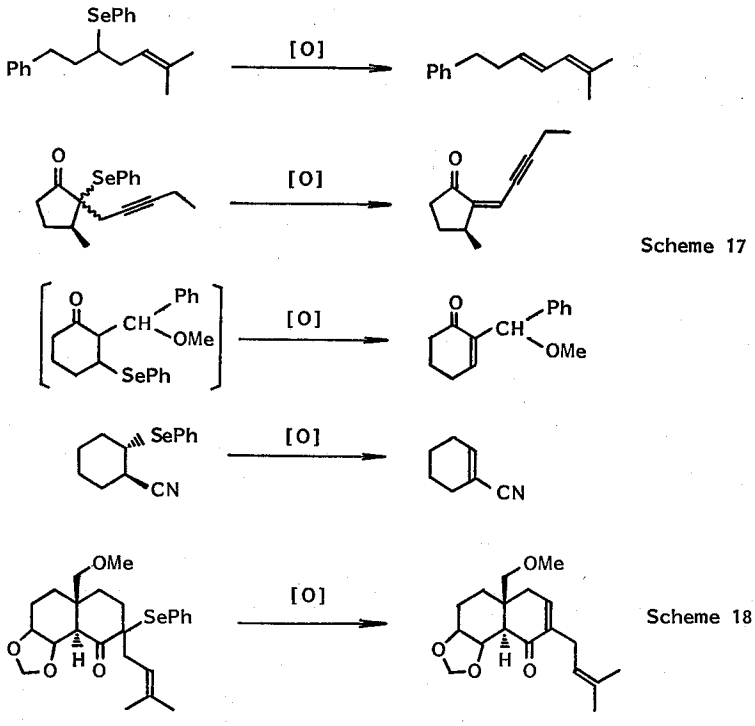


Scheme 15



Scheme 16

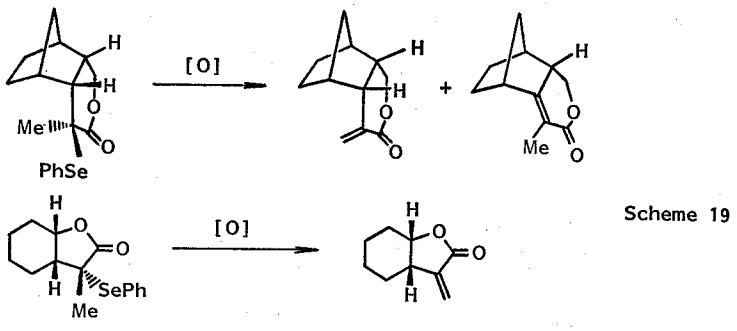
is favored presumably due to the instability of α-methylene ketones (Scheme 16). It has been reported that the selenoxide elimination proceeds regioselectively when an introduced double bond is conjugated with such groups as carbon-carbon double bond,[8] carbon-carbon triple bond,[43] carbonyl group,[45] and cyano group[46]. The formation of non-conjugated compounds was not observed even in the case where an enone formation suffers from a steric hindrance (Scheme 17). Interestingly, the formation of endocyclic enone, not conjugated with olefin on a side chain, has been reported (Scheme 18)[47]. The *syn* nature of the selenoxide elimination sometimes plays an important role in determining the direction of the elimination. Grieco *et al.* have observed the formation of a mixture of α-methylene lactone and the corresponding endocyclic double bond isomer when the relationship between the α-phenylseleno group



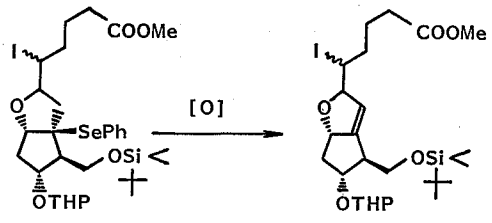
Scheme 17

Scheme 18

and the ring proton β to the lactone carbonyl is *syn*. A selective formation of the desired α-methylene lactone was achieved by establishing the *anti* relationship between the α-phenylseleno group and the β-hydrogen (Scheme 19).[48] This technique was utilized in a selective formation of dihydorfuran ring in the synthesis of a furan prosta-

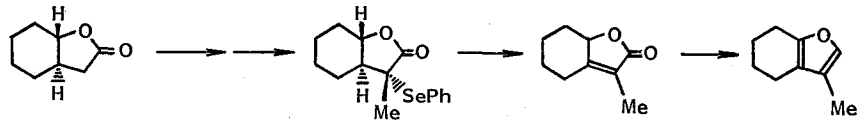


Scheme 19



Scheme 20

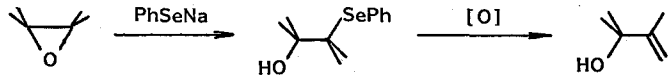
cyclin analogue (Scheme 20).[49] The formation of a substituted furan ring by the selective introduction of an endocyclic double bond realized by the control of stereochemistry has also been reported (Scheme 21).[50]



Scheme 21

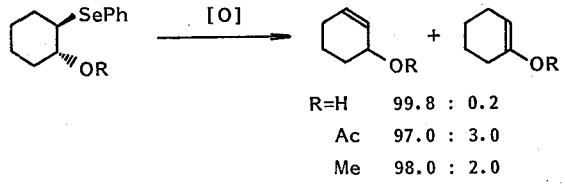
6.2 Oxygen Substituent

As briefly mentioned in section 5.1, the selenoxide elimination with a hydrogen atom attached to the carbon atom bearing an alkoxy group is extremely slow. Sharpless *et al.*[51] have examined the oxidative elimination of β-hydroxyalkyl phenyl selenide for the first time and discovered that allylic alcohols were produced selectively. This reaction was utilized in the conversion of epoxides to allylic alcohols (Scheme 22).

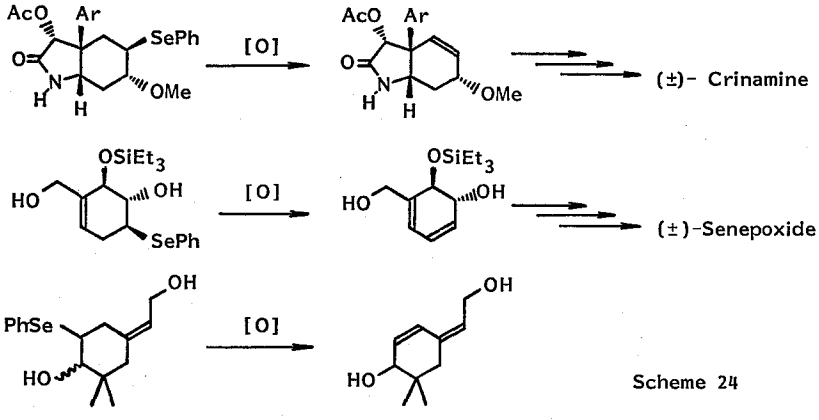


Scheme 22

Successively, the same authors have examined the regioselectivity of the selenoxide elimination of β-hydroxy-, β-acetoxy-, and β-methoxy-cyclohexyl phenyl selenoxides.[52] As shown in Scheme 23, the elimination away from an oxygen functional group was strongly favored in all cases. This indicates that numerous examples of the preparation of β-oxyalkyl phenyl selenides[1~3,53] can open up a way to synthetically valuable allylic



Scheme 23

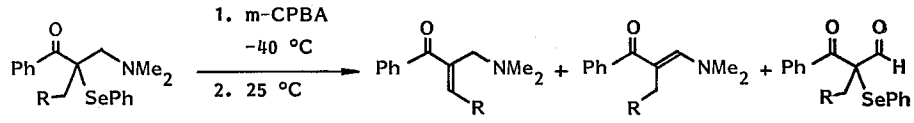


Scheme 24

alcohol derivatives. The reaction has been utilized in the total synthesis of numerous natural products such as (±)-crinamine[54] and (±)-senepoxide,[55] and also in the synthesis of a diol component of the red alga ochtodes crockeri[56] (Scheme 24).

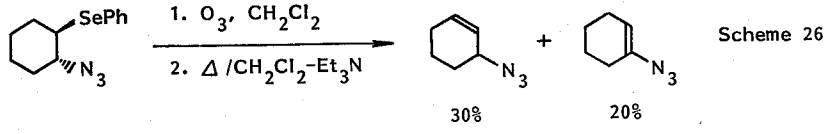
6.3 Nitrogen Substituent

The selenoxide elimination of alkyl aryl selenides bearing a nitrogen functional group at β position of an alkyl chain is not generally regioselective in contrast with the case of an oxygen functional group. The selectivity depends on the nature of the nitrogen functional group. Dimethylamino group was first examined and reported to exert a much less pronounced control of elimination as compared to the oxygen functional group.[57] As shown in Scheme 25, an elimination away from a dimethyl-



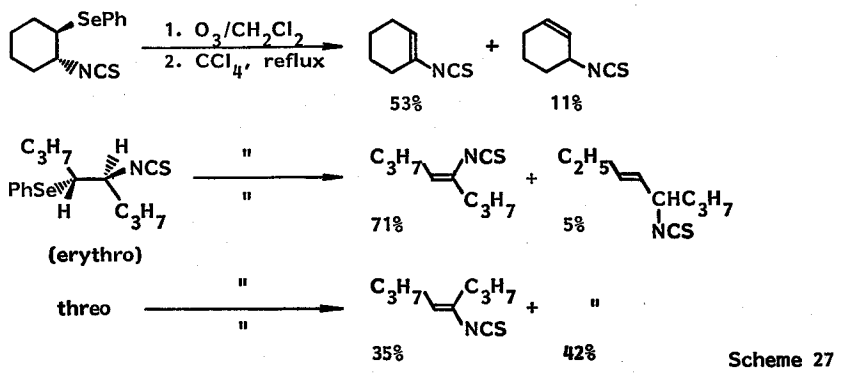
	R=H	84%	< 2%	5%
Scheme 25	Me	54%	20%	10%

amino group is strongly favored when a hydrogen atom in a methyl group is to be eliminated (R=H). By the introduction of a methyl group (R=Me), an enamine is formed in a comparable amount (30%) to an allylic amine (a saturated product is formed *via* the addition of selenium reagent to the produced enamine). This indicates that a methyl group retards the elimination toward a carbon as effective as a dimethylamino group. The effect of an azide group seems to be almost the same to that of a dimethylamino group. Although an allylic azide is the major elimination product, the formation of its regioisomeric vinyl azide is slightly favored than the statistically expected amount (Scheme 26).[58] The conjugation of a double bond with an azide

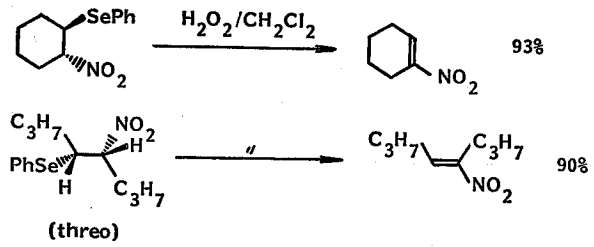


Scheme 26

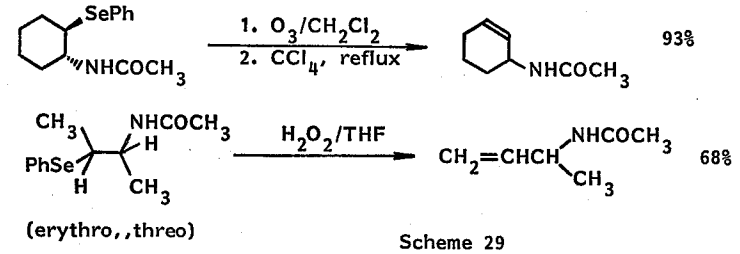
group might be one reason for that. The elimination toward a nitrogen functional group is much favored in the case of β-isothiocyanatoalkyl phenyl selenoxides.[59] The formation of vinyl isothiocyanates predominates except the case of E-4-isothiocyanatooct-4-ene which is unstable due to the steric hindrance and slowly isomerizes to Z-isomer (Scheme 27). Conjugated nitroalkenes were produced selectively by the oxidative elimination of β-nitroalkyl phenyl selenides.[60] A strong conjugation effect as well as the increased acidity of α-hydrogen may contribute to this high regioselectivity and, interestingly, E-4-nitrooct-4-ene was produced selectivly in a good yield (Scheme 28). Another example of the regioselective selenoxide elimination controlled by a nitrogen functional group is the case of β-acetamidoalkyl phenyl selenides. In contrast with the nitro group described above, the elimination away from an acetamido group proceeded selectively to afford allylic amides (Scheme 29).[26,27] The reason for this



Scheme 27



Scheme 28

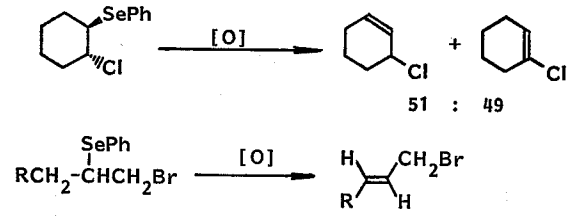


Scheme 29

contrast effect between dimethylamino and acetamido groups described above has not yet been clarified.

6.4 Halogen Substituent

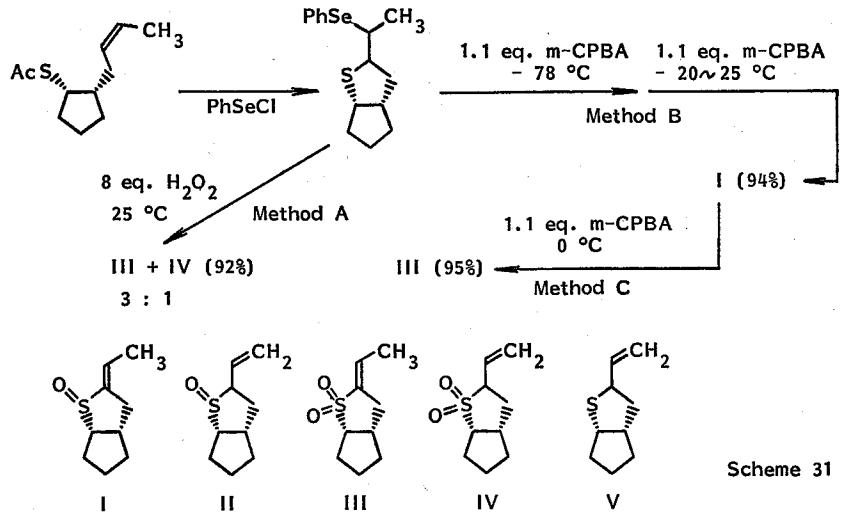
It has been reported that the chlorine atom at β position of ethyl phenyl selenoxide slightly increases the rate of the selenoxide elimination. In agreement with this, the oxidative elimination of β-chlorocyclohexyl phenyl selenide affords an equal amount of allylic and vinylic chlorides.[52] On the other hand, allylic bromides were produced selectively by the oxidative elimination of β-bromoalkyl phenyl selenides[61] (Scheme 30).



Scheme 30

6.5 Sulfur Substituent

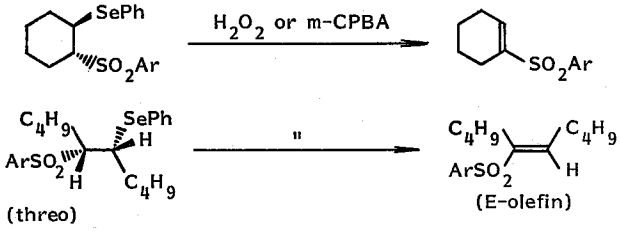
The regioselectivity of the selenoxide elimination bearing a sulfur substituent at β position of an alkyl group was first examined by Nicolaou *et al.*,[62] the results of which being summarized in Scheme 31. By the use of an excess of hydrogen peroxide



Scheme 31

(Method A), a mixture of regioisomers of sulfones, III and IV, was obtained, indicating that the elimination proceeded to both directions. When a stoichiometric amount of m-CPBA was used stepwise by controlling the reaction temperature (Method B), only a vinylic sulfoxide, I, was produced. Further oxidation after Method B (Method C) gave a conjugated sulfone, III, as a sole product in a high yield. These results were interpreted by assuming that in Method B sulfur was oxidized to sulfoxide prior to the selenoxide elimination, while the selenoxide elimination and the oxidation of sulfide to sulfoxide were competing in Method A. Thus, in the latter case, the selenoxide elimination of β-sulfoxide afforded a conjugated vinylic sulfoxide (I) selectively, while that of β-sulfide gave a non-conjugated allylic sulfide (V) which was further oxidized to IV *via* II.

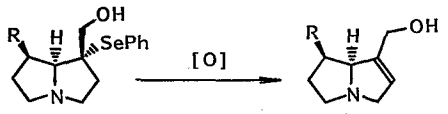
Two research groups have investigated the regioselectivity of the oxidative elimination of β-phenylseleno sulfones.[63,64] As shown in Scheme 32, a conjugated vinylic sulfone was produced in a good yield, none of non-conjugated allylic isomers being detected in all cases examined.



Scheme 32

6.6 Miscellaneous Effect

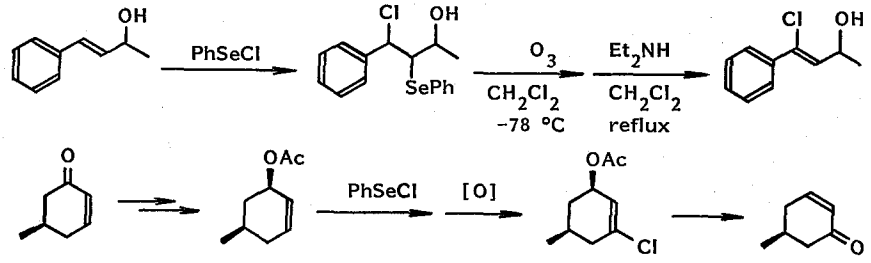
The selenoxide elimination has been utilized in the synthesis of a necine base which is contained in the biologically active pyrrolizidine alkaloids. The elimination step in the sequence to retronecine (R=OH)[65] and spinidine (R=H)[66] is shown in Scheme 33. The configuration of a phenylseleno group is considered to be *syn* to



Scheme 33

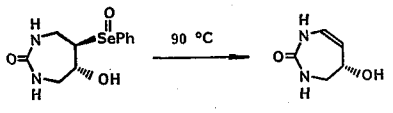
a bridgehead hydrogen on the basis of a steric hindrance in the introduced step of a phenylseleno group. Among the two possible regioisomeric allylic alcohols only one isomer was produced selectively. This was attributed to an electron-withdrawing effect of a nitrogen atom, the elimination away from which is known to be moderately favored (see section 6.3), and also maybe to the instability of the other isomer which should have a bridgehead double bond.

As has already been mentioned, the selenoxide elimination with a hydrogen geminal to a chlorine atom is slightly favored than the statistically expected amount (section 6.4), while that with a hydrogen geminal to an oxygen functional group is strongly disfavored (section 6.3). As can be expected from these facts, vinyl chloride derivatives were produced selectively by the oxidative elimination of alkyl phenyl selenides bearing hydroxy (or acetoxy) and chlorine substituents at respective β-carbons.[67] Combined with the same authors' findings that the addition of phenylselenenyl chloride to allylic alcohol derivatives proceeds regioselectively, this regioselective selenoxide elimination was utilized in the 1,3-carbonyl transposition reactions as shown in Scheme 34.



Scheme 34

In the selenoxide shown in Scheme 35 a hydroxy group and an amide group are situated on different β-carbons respectively. Since both substituents have been reported to force the elimination away from themselves to afford the allylic compounds (sections 6.2 and 6.3), this is a good example to compare the effectiveness of the two

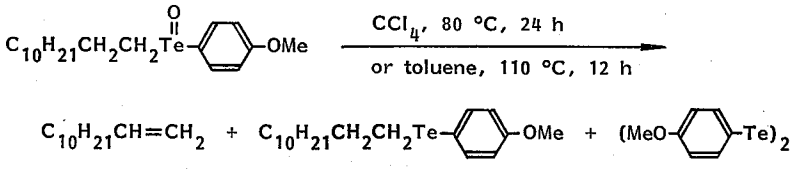


Scheme 35

groups for regiochemistry of the elimination. The reaction proceeded at 90°C to give a vinylic amide derivative selectively, indicating that a hydroxy group is more effective than an amido group in determining the direction of the elimination.[68]

7. The Telluroxide Elimination

In contrast to the selenoxide elimination described so far leading to a double bond formation, little is known on the telluroxide elimination.[69] Original work has been done by Sharpless *et al*,[20] who reported the formation of mixtures of olefins and/or alcohols by t-BuOOH oxidation of several organic tellurides in benzene without isolation of the corresponding telluroxides (see section 3, Scheme 5). Cava *et al.*[70] clarified that n-dodecyl 4-methoxyphenyl telluroxide is stable and its decomposition to 1-dodecene and the corresponding telluride occurs only in refluxing CCl_4 or toluene for a long time (Scheme 36). Recently, it was found that it is not necessarily the case

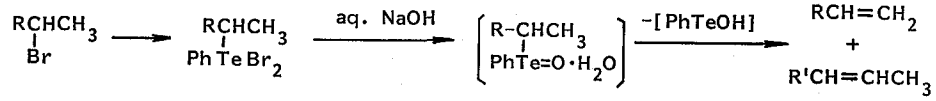


Scheme 36

for all telluroxides and, in fact, *sec*-alkyl phenyl telluroxides decompose readily to afford olefins, allylic alcohols, and allylic ethers in high yields under very mild conditions.[4] The telluroxide elimination, therefore, may be utilized in olefin and allylic compound syntheses, a reaction which previously appeared to be of little value.

7.1 The Treatment of Alkylphenyltellurium Dibromide with aq. NaOH[4]

The treatment of *sec*-alkylphenyltellurium dibromide with aqueous 0.5 N NaOH at room temperature readily afforded a mixture of the corresponding olefins in 70–80% yields together with small amounts of alcohol and ketone (Scheme 37). The reaction

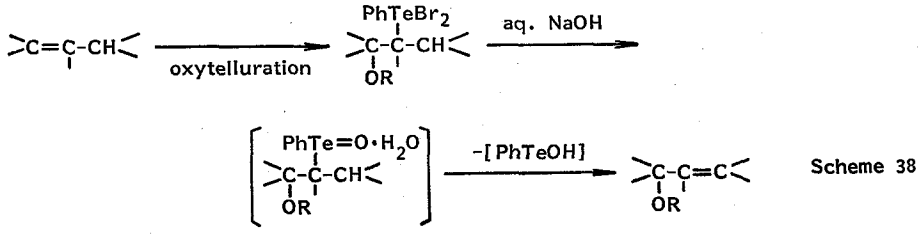


Scheme 37

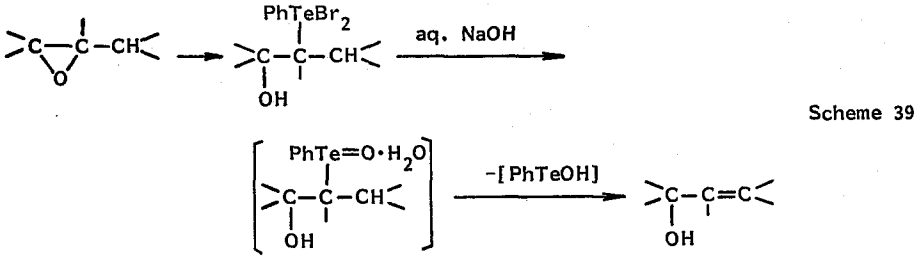
proceeds *via* the formation of telluroxide[28] followed by the telluroxide elimination. As to the formation of linear olefins, the ratio of terminal to internal olefins (2.5/1; when R=n-C_6H_{13} and R=n-C_8H_{17}) is higher than that observed in the selenoxide and sulfoxide eliminations of 2-butyl phenyl selenoxide (1.56/1),[16] 2-(4-phenylbutyl) phenyl selenoxide (1.78/1),[16] and 2-butyl phenyl sulfoxide (1.5/1),[71] respectively. Namely, the telluroxide elimination under this condition shows more preference for elimination toward the less substituted carbon than the selenoxide and sulfoxide eliminations where the ratio of terminal to internal olefins seems to be governed statis-

tically by the number of hydrogen (CH_3 *vs.* CH_2). Similar facile telluroxide elimination was also observed to give the corresponding olefin by starting from cycloheptyl, cyclooctyl, and cyclododecyl bromides.

When this procedure was combined with the oxytelluration of olefins,[72] allylic ethers were readily obtained from internal olefins (Scheme 38). The yield at the elimination step was over 80%. Similarly, allylic alcohols were obtained from (β-hydroxyalkyl)tellurium compounds that are prepared by ring opening of the corresponding epoxides (Scheme 39).

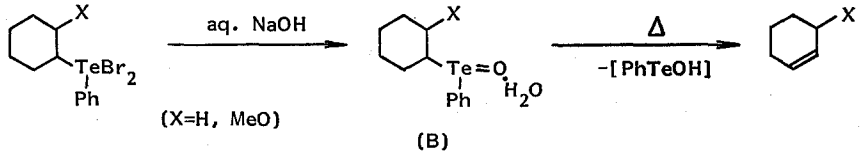


Scheme 38



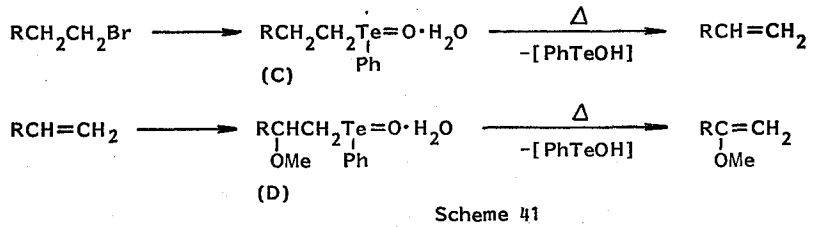
Scheme 39

In contrast with other cyclic systems, the cyclohexyl system was exceptional. Thus, cyclohexyl and 2-methoxycyclohexyl phenyl telluroxides (B) were isolated, respectively, as very stable compounds by a similar treatment, and the telluroxide elimination hardly occurred under this condition (Scheme 40). In these cases the pyrolysis at 200–220°C gave the expected cyclohexene and 3-methoxycyclohexene, respectively.



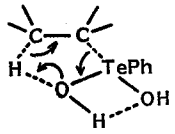
Scheme 40

Contrary to observations for the above described *sec*-alkyl phenyl telluroxides, n-alkyl analogues such as (C) and (D), prepared by a similar way as above, were stable compounds as reported by Cava *et al.* (Scheme 41).[70] The pyrolysis of these compounds at 200–240°C afforded the corresponding olefins and vinylic ethers in good yields as in the case of the cyclohexyl analogue (B).



Scheme 41

The selenium analogues of (B), (C), and (D) could not be isolated and instead gave readily olefins *via* the selenoxide elimination as described so far. The telluroxides' lesser reactivity for elimination seems to be as follows. (1) All the "telluroxides" were isolated as their hydrates and are almost certainly dihydroxy telluranes in which the tellurium is four-coordinate as shown in (E). In this form the basicity of oxygen for

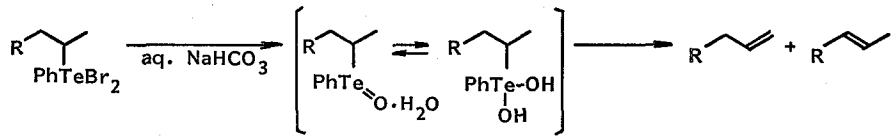


(E)

hydrogen may be reduced and the elimination should be slower compared to the selenoxides, which have a smaller tendency to add water. (2) The longer bond lengths (C-M and M-O, M=Te, Se) in telluroxide than in selenoxide may place the oxygen far away from the appropriate hydrogen to be eliminated as has been proposed by Sharpless *et al.*[20]

7.2 The Treatment of Alkylphenyltellurium Dibromide with aq. $NaHCO_3$[73]

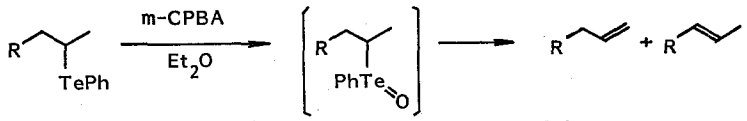
In the treatment of the dibromide with aq. NaOH, it might be possible that β-hydrogen is abstracted at first followed by the elimination of tellurium moiety (E_2 elimination). In order to know whether the elimination proceeds *via* E_2 process, the same dibromides were treated with a much weaker base, aq. $NaHCO_3$, at room temperature. The reaction was slower (*ca.* 15 h) and yet nearly the same products, yields, and isomer ratios were obtained as in the case of aq. NaOH treatment (Scheme 42). Since it is not conceivable that β-hydrogen can be abstracted by such a weak base, the result supports the reaction pathway of the initial formation of the telluroxides followed by its elimination (probably E_i elimination) in the treatment with either aq. NaOH or aq. $NaHCO_3$.



Scheme 42

7.3 The Oxidation of Alkyl Phenyl Telluride with m-CPBA[74]

Recently, it was disclosed that the teratment of *sec*-alkyl phenyl telluride with 1 equivalent of m-CPBA in diethyl ether or ethyl acetate at room temperature resulted in the telluroxide elimination to form olefins as main products in over 60% yield together with small amounts of alcohol and ketone (Scheme 43). The ratio of terminal



Scheme 43

to internal olefins obtained from 2-alkyl phenyl telluride was 1.5-1.7/1, the result being slightly different from that in an alkaline treatment and nearly the same as that of selenoxide and sulfoxide eliminations. It is not yet clear whether the slight difference of this ratio is due to a structural difference of the telluroxide (F) from its hydrate form such as (E). Much work on the telluroxide elimination is awaited from both mechanistic and synthetic points of view.

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