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# REACTIONS OF SELENOXIDES:
# THERMAL SYN-ELIMINATION AND $H_2{}^{18}O$ EXCHANGE.

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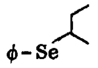
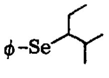
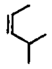
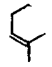
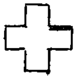
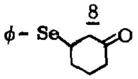
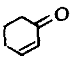
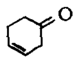
During their synthesis of a chiral steroidal selenoxide, Jones and co-workers discovered the selenoxide analog of the sulfoxide syn-elimination reaction.[1] In the case reported by these authors, the selenoxide decomposed to olefin even at 0°. Because of our interest in the development of new selenium reagents for organic synthesis,[2] we wished to know more about this gentle olefin forming process. We have prepared a variety of alkyl phenyl selenoxides and have found that they all decomposed readily to olefins at room temperature (Table I).

Table I. Selenoxide Decomposition [a)]

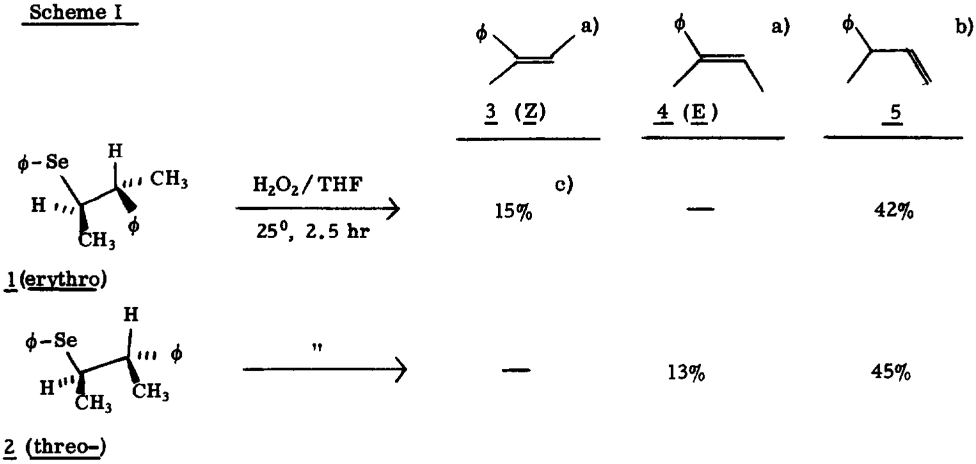
| Selenide [b)] | Olefins (ratio) | | | Total yield (%) |
|---|---|---|---|---|
|  6 |  (61) |  (28) |  (11) | 71 |
|  7 |  (79) |  (7) |  (14) | ~ 100 |
|  8 |  (50) |  (50) | | 94 |
|  9 |  (100) |  (0) | | 95 |

a) The selenide was dissolved in THF, and excess (10 equiv.) of 70% $H_2O_2$ was added while cooling in an ice bath. Upon completion of oxidation, as determined by TLC, the reaction mixtures were then allowed to stand at room temperature for 3 hrs. Yields and product ratios were determined by glc, relative to an internal standard.

b) The selenides were prepared by reaction of the corresponding tosylate (7), halide (6, 8) or unsaturated ketone (9) with ϕSeNa in ethanol (for a convenient preparation of this reagent see ref. 2c). They are all new compounds (except 6) and have been characterized by analytical and spectral means.

The syn- nature of the elimination was proven unambiguously by applying the sequence used by Cram for determining the stereochemistry of the amine oxide and related pyrolytic eliminations.[3] The erythro- (1) and threo- (2) phenyl selenides were prepared by reaction of the corresponding tosylates[4] with the sodium salt of selenophenol[2C] in ethanol. Oxidation of the diastereomeric selenides 1 and 2 to the corresponding selenoxides was effected with excess (10 equiv.) 70% $H_2O_2$ in tetrahydrofuran. As revealed in Scheme I, formation of the 2-phenyl-2-butenes occurred by stereospecific syn- elimination. The erythro- isomer 1 gave only the Z-olefin 3, and the threo- isomer 2 gave only the E-olefin 4, while the major product in both cases was 3-phenyl-1-butene 5.

Scheme I



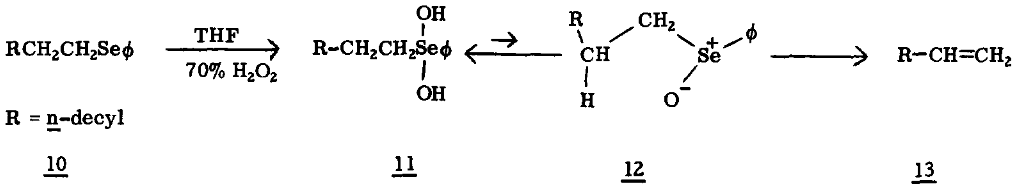
a) A mixture of olefins 3 and 4 was prepared by Wittig reaction of ethylidene triphenyl phosphorane with acetophenone. The higher boiling isomer is known (ref. 3b) to be E olefin 4.
b) Prepared via Wittig reaction from 2-phenyl propanal.
c) These are absolute yields determined by glc relative to an internal standard. All three olefins were resolved by a 6' x 1/8" 10% UC-W98/ Chromosorb W column at 100°. The relative retention times were 4 > 3 > 5.

Examination of the examples in Table I reveals the close similarity between the olefin mixtures obtained from selenoxide eliminations and those obtained from the mechanistically related eliminations of amine oxides[5] and sulfoxides.[6] The olefin mixtures obtained from the oxidations of selenides 6 and 7 (Table I) are clearly not those expected from a process having $E_1$ or $E_2$ character.

The difficulty of obtaining chiral selenoxides has been reasonably attributed to their ready racemization through an achiral hydrate.[1,7] We have made several observations which further support the importance of hydrates in selenoxide chemistry.

The primary selenide 10 did not behave like the secondary selenides (Table I) upon oxidation with $H_2O_2$; after 16 hr. at room temperature only 6% of the expected olefin 13 had formed.

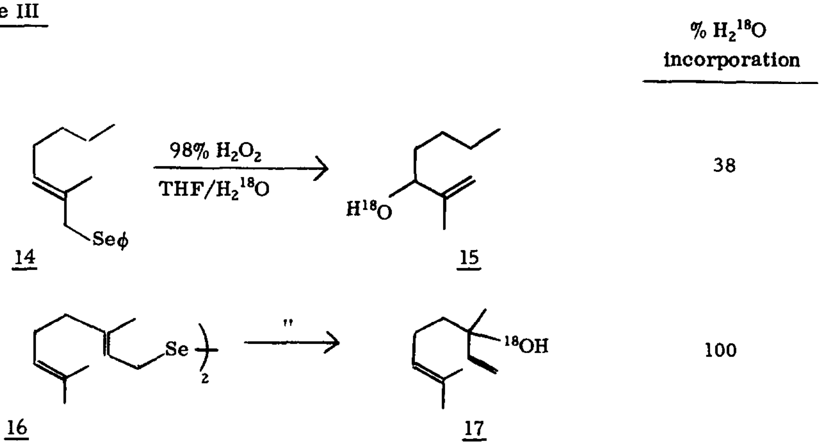
Scheme II



If, however, excess anhydrous $MgSO_4$ was added shortly after $H_2O_2$ addition was complete, olefin 13 was formed in 77% yield after only 2.5 hr. at room temperature. In this case, it would appear that the hydrate 11 is actually the predominant species in solution. The dehydrating agent ($MgSO_4$) shifts the equilibrium toward the selenoxide 12.

Finally, the experiments outlined in Scheme III indicate that $H_2{}^{18}O$ exchange of the

Scheme III



selenoxide and seleninic acid derived from **14** and **16** respectively occurs at a rate comparable to the rapid [2,3] sigmatropic rearrangements[2a] leading to the observed products (**15** and **17**).

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4) Cram's procedure (ref. 3a) for preparation of the 2-tosyloxy-3-phenyl butanes was followed except that we prepared the racemic *erythro* (mp 39–41°) and *threo* (mp 46-47°) tosylates and not the resolved tosylates. Of course, the *erythro*-tosylate gives rise to the *threo*-selenide **2** and *vice-versa.*

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