our results suggest that the state responsible for ethylenediamine aquation is $^4B_2$, whereas that responsible for Cl^- and SCN^- aquation is the lowest quartet, ^4E. This is in agreement with the expectations based on the MO approach,[16-18] according to which in our complex the $^4B_2$ excited state corresponds to the population of a σ-antibonding MO having predominant $d_{x^2-y^2}$ character, whereas the lowest ^4E state corresponds to the population of a σ-antibonding MO having predominant d_{z^2} character.

(16) D. S. McClure in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 498.
(17) W. W. Fee and J. N. MacB. Harrowfield, *Aust. J. Chem.*, 23, 1049 (1970).
(18) D. A. Rowley, *Inorg. Chem.*, **10**, 397 (1971).

M. T. Gandolfi, M. F. Manfrin, L. Moggi, V. Balzani*
Istituto Chimico "G. Ciamician" dell'Università
Laboratorio di Fotochimica e Radiazioni
d'Alta Energia del C.N.R.
Bologna, Italy
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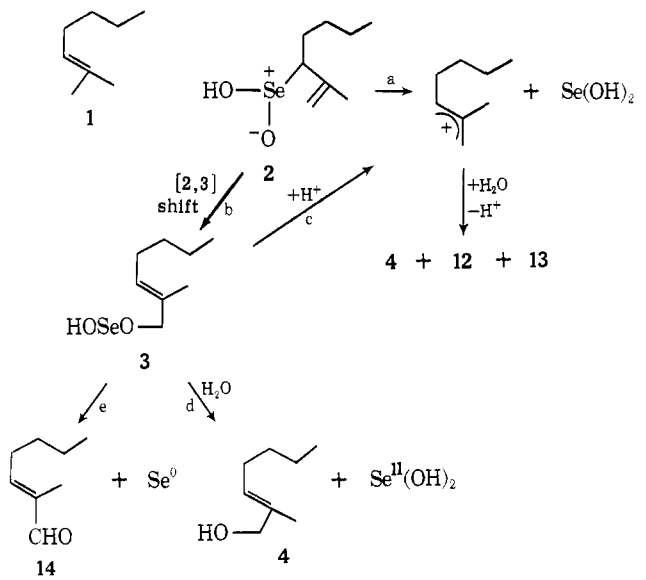
Selenium Dioxide Oxidation of Olefins. Evidence for the Intermediacy of Allylseleninic Acids

Sir:

In spite of considerable study[1] the mechanism of allylic oxidation of olefins by selenium dioxide remains controversial. Wiberg and Nielsen[2] favor initial formation of an allylseleninic acid (**2**) which then undergoes solvolysis to products (path a, Scheme I). Schaefer[3] and Trachtenberg,[4] both of whom have proposed different mechanisms not shown in Scheme I, argue against the involvement of allylseleninic acids (**2**) because of the known inertness of benzylseleninic acid to solvolysis. However, a [2,3] sigmatropic rearrangement (path b, Scheme I) of the allylseleninic acid (**2**) to a selenium(II) ester (**3**) occurred to us as a likely alternative to the solvolytic pathway a. We now report evidence which strongly suggests that the [2,3] sigmatropic shift indicated in path b is a facile process. The required rearrangement (path b) is well known for allylic sulfinates[5] and especially allylic sulfoxides,[6] but the equilibrium usually lies heavily in favor of the sulfur(IV) derivative. In the case of the selenium analogs (*e.g.*, **2** and **3**) it seemed likely that the selenium(II) derivative **3** would be more stable. Significantly, in contrast to the well known alkyl-, aryl-, and benzylseleninic acids and selenoxides[7] there are no reports of allyl analogs.

Scheme I[a]



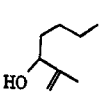
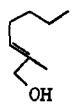
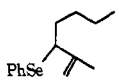
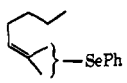
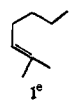
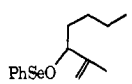
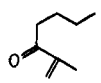
[a] For convenience, the specific case for 2-methyl-2-heptene is illustrated, but the scheme is meant to apply to olefins in general.

A standard method for preparation of seleninic acids involves oxidation of a diselenide with hydrogen peroxide.[7] Attempts to prepare geranylseleninic acid (**6**) by oxidation of geranyl diselenide (**5**)[8] led to the results outlined in Table I (experiments 1–4). In experiments 1, 2, and 3 geranylseleninic acid (**6**) may[9] be formed but it rearranges rapidly to the selenium(II) ester of linalool (analog of **3**) which hydrolyzes (path d, Scheme I) to linalool (**f**) under the reaction conditions. Although the quantitative incorporation of solvent water (experiment 2) might suggest an SN1 (path c), the fact that no methyl ethers are formed in tetrahydrofuran–methanol (experiment 3) using 98% H_2O_2 indicates that ^{18}O must enter by rapid exchange of the seleninic acid **6** prior to rearrangement. Geranylselenol (**8**),[8,10] geranyl monoselenide (**9**),[8] and geranyl linalyl selenide (**10**)[8] (experiments 5, 6, and 7, respectively) upon oxidation gave the alcohols expected from [2,3] rearrangement of the respective C=CCSe$^+$O$^-$ moieties followed by hydrolysis (paths b and d).

Büchi and Wüest established that selenium dioxide[11] selectivity attacks trisubstituted olefins such as **1** to give only the (*E*)-alcohol **4**. If our proposed mechanism is correct, then the sigmatropic rearrangement of the allylseleninic acid **2** must lead stereoselectively to the (*E*)-ester **3**. In order to test this hypothesis the allyl phenyl selenides **11** and **15** were prepared.[8,12]

(1) For two recent reviews, see: E. N. Trachtenberg in "Oxidation," Vol. 1, R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 3; and R. A. Jerussi in "Selective Organic Transformations," Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 6, p 301.
(2) K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, **29**, 3353 (1964).
(3) J. P. Schaefer, B. Horvath, and H. P. Klein, *ibid.*, **33**, 2647 (1968).
(4) E. N. Trachtenberg, C. H. Nelson, and J. R. Carver, *ibid.*, **35**, 1653 (1970).
(5) Q. E. Thompson, *ibid.*, **30**, 2703 (1965).
(6) P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4869 (1968); D. A. Evans, G. C. Andrews, and C. L. Sims, *ibid.*, **93**, 4956 (1971).
(7) J. D. McCullough and E. S. Gould, *ibid.*, **71**, 764 (1949).
(8) All the organoselenium compounds described in this communication are new compounds and have been adequately characterized by analytical and spectral data. A brief outline of their preparations is as follows: **5** and **9** by the reaction of Na_2Se_2 and Na_2Se, respectively, with geranyl chloride; **11** by the action of C_6H_5SeNa on the corresponding chloride; **8** by LAH reduction of the corresponding selenocyanate, which in turn was obtained by treating KSeCN with geranyl chloride; **10** by treatment of **5** with $(C_6H_5)_3P$; and **15** by thermal rearrangement of **11**. A more complete discussion of these syntheses appears elsewhere: K. B. Sharpless and R. F. Lauer, submitted for publication.
(9) We cannot be sure the seleninic acid (**6**) actually forms since the [2,3] shift could occur before complete oxidation occurs (*e.g.*, at the selenoselinate stage). Baldwin and coworkers have reported such a rearrangement in the case of diallyl thiosulfinates [J. E. Baldwin, G. Hofle, and Se Chun Choi, *J. Amer. Chem. Soc.*, **93**, 2810 (1971)].
(10) Selenol **8** was added to excess H_2O_2 so as to favor direct (*i.e.*, not *via* **5**) oxidation to **6** (experiment 5).
(11) G. Büchi and H. Wüest, *Helv. Chim. Acta*, **50**, 2440 (1967). The stereochemistry established by Büchi enabled Rapoport to use SeO_2 in the last step of a sirenin synthesis [J. J. Plattner, U. T. Bhalerao, and H. Rapoport, *J. Amer. Chem. Soc.*, **91**, 4933 (1969)].
(12) All attempts to prepare the selenol and diselenide analogs of **11** failed.[8] Thus, we had to be content with studying the rearrangement of the allyl phenyl selenoxide **16** rather than the desired allylseleninic acid **2**.

Table I

Reactant	Reagent[a]	Solvent[b]	Products (% yield)[c] Linalool (7)	Geraniol	Nerol	Limonene
1. Geranyl diselenide (5)	$3H_2O_2$	THF-H_2O	78			
2. Geranyl diselenide (5)	$3H_2O_2$	THF-$H_2{}^{18}O$	75 (100% $H_2{}^{18}O$ incorporation)			
3. Geranyl diselenide (5)	$3H_2O_2$	THF-CH_3OH	75 (no methyl ethers)			
4. Geranyl diselenide (5)	$3H_2O_2$	Et_2O	41	18	8	7
5. Geranylselenol (8)	$10H_2O_2$	THF-H_2O	80			
6. Geranyl monoselenide (9)	$3H_2O_2$	THF-H_2O	70			
7. Geranyl linalyl monoselenide (10)	$3H_2O_2$	THF-H_2O	36	22	14	
			 12	 4	 13	 14
8.  11[d]	$1H_2O_2$	THF-CH_3OH	14	71	<1	5
9.  15	$1H_2O_2$	THF-CH_3OH	100	<1		
10.  1[e]	SeO_2	95% EtOH	3	92	5	
11.  17		$CHCl_3$	 18			

[a] The oxidations were performed at 0–25° by addition of 98% H_2O_2. [b] The cosolvent systems consisted of THF with equal volumes of either H_2O or dry CH_3OH. [c] Yields were determined by glc using internal standards. [d] Contaminated with 6% of the *E* and *Z* isomers of **15**. [e] According to Büchi's procedure (ref 11).

Oxidation of these selenides (experiments 8 and 9) resulted in high yields of the rearranged alcohols. More importantly, selenide **11** gave only the (*E*)-alcohol **4**. Oxidation of olefin **1** with SeO_2 followed by borohydride reduction[11] (experiment 10) gave principally (*E*)-alcohol **4** but glpc analysis revealed some of the (*Z*)-alcohol **13** and the secondary isomer **12**. Thus, rearrangement of the selenoxide **16** derived from **11** leads even more selectively to the (*E*)-alcohol **4** than the selenium dioxide oxidation itself (experiment 10). Grieco has just reported[13] the same stereospecificity for the sigmatropic rearrangement of the sulfur analog of **16**.

Selenate ester **17**, formed by reaction of alcohol **12** with C_6H_5SeBr in the presence of AgOAc,[14] decomposed at room temperature to ketone **18** (experiment 11). By contrast, the analogous sulfonate esters rearrange rapidly to the sulfoxides.[6] This result suggests that the carbonyl products formed in SeO_2 oxidations may in part arise directly from the selenium(II) ester (path e, Scheme I).

With the exception of experiment 4, where involvement of path c seems likely,[15] most of the products in Table I appear to derive from hydrolysis of the Se–O bond in the selenium(II) ester (path d). The mild conditions employed for these oxidations (0–25°) are no doubt responsible for suppression of path c which would be favored at the higher temperatures (70–100°) usually required in SeO_2 oxidations. The ease with which phenyl allyl selenides undergo oxidation–rearrangement, in high yield, to allylic alcohols suggests synthetic applications which we are pursuing.

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K. B. Sharpless,* R. F. Lauer
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
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(13) P. A. Grieco, *Chem. Commun.*, 702 (1972).
(14) According to the procedure of H. Rheinboldt, "Methoden der Organischen Chemie," H. Weyl, Ed., 4th ed, Vol. 9, Georg Thieme Verlag, Stuttgart, 1955, p 1176.
(15) Actually small amounts (2–10%) of geraniol, nerol, and limonene were also observed in experiments 1, 2, 3, 5, and 6.

Reactions of π-Allylnickel Bromide Complexes with Conjugated Systems. I. Reaction with Quinones. The Synthesis of Coenzyme Q_1 and Plastoquinone-1

Sir:

We report here a new and unusual reaction, the alkylation of quinones by π-allylnickel bromide com-