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FORMATION OF 3-(*m*-CHLOROBENZOYLOXY)-2-(PHENYLSELENO)PROPAN-1-OL AND 2-(*m*-CHLOROBENZOYLOXY)-3-(PHENYLSELENO)PROPAN-1-OL FROM A REACTION OF ALLYL PHENYL SELENIDE WITH *m*-CHLOROPEROXYBENZOIC ACID

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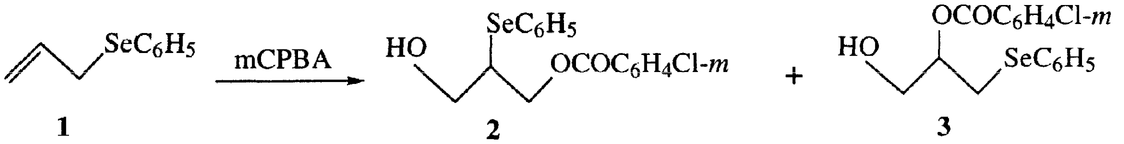
Abstract. Oxidation of allyl phenyl selenide with *m*-chloroperoxybenzoic acid unexpectedly afforded two compounds, the structures of which were determined as 3-(*m*-chlorobenzoyloxy)-2-(phenylseleno)propan-1-ol and 2-(*m*-chlorobenzoyloxy)-3-(phenylseleno)propan-1-ol. Structure determination of the products is described and the possible mechanisms are discussed.

[2,3]Sigmatropic rearrangement of allylic selenoxides to produce allylic selenenates followed by hydrolysis to produce allylic alcohols, is the generally accepted mechanism for the formation of allylic alcohols by oxidation of allylic selenides. [1] The archetypal allyl phenyl selenide is the same in that it affords allyl alcohol when oxidized with hydrogen peroxide in the presence of pyridine. [2]

However, we have found that the oxidation of allyl phenyl selenide (**1**) with *m*-chloroperoxybenzoic acid unexpectedly gives a mixture of two products which still contain a selenium atom. Their structures were elucidated as 3-(*m*-chlorobenzoyloxy)-2-(phenylseleno)propan-1-ol (**2**) and 2-(*m*-chlorobenzoyloxy)-3-(phenylseleno)propan-1-ol (**3**). This paper reports the unusual results and presents some discussions on the mechanism of the reaction.



Oxidation of allyl phenyl selenide (**1**) [3] with *m*-chloroperoxybenzoic acid was carried out using 10 mmol of allyl phenyl selenide and 15 mmol of *m*-chloroperoxybenzoic acid in dichloromethane at room temperature. The reaction was completed within 2 h. The products obtained were then separated by chromatography to afford two compounds [together with a hydrolyzed compound, 2-(phenylseleno)propane-1,3-diol, identified later], both of which showed the presence of a *m*-chlorobenzoyl group in their infrared and ^{1}H NMR spectra. [4] The yields were 47 and 14% for **2** and **3**, respectively. (In addition, 9% of **1** was recovered and 7% of the diol obtained.)

Examination of the connectivity indicated that there is a sequence of HO-CH_2-CH-CH_2 in both **2** and **3**. Protons in both the CH_2 groups were diastereotopic. Because both compounds were oily, we hydrolyzed the ester moiety and then converted the obtained diols (**4** and **5**) to 3,5-dinitrobenzoate (**6** and **7**). The major compound afforded crystals that were suitable for X-ray crystallography. The results are shown in Fig. 1 as an ORTEP drawing. [5] Its structure is 1,3-bis(3,5-dinitrobenzoyloxy)-2-(phenylseleno)propane (**6**). Thus the

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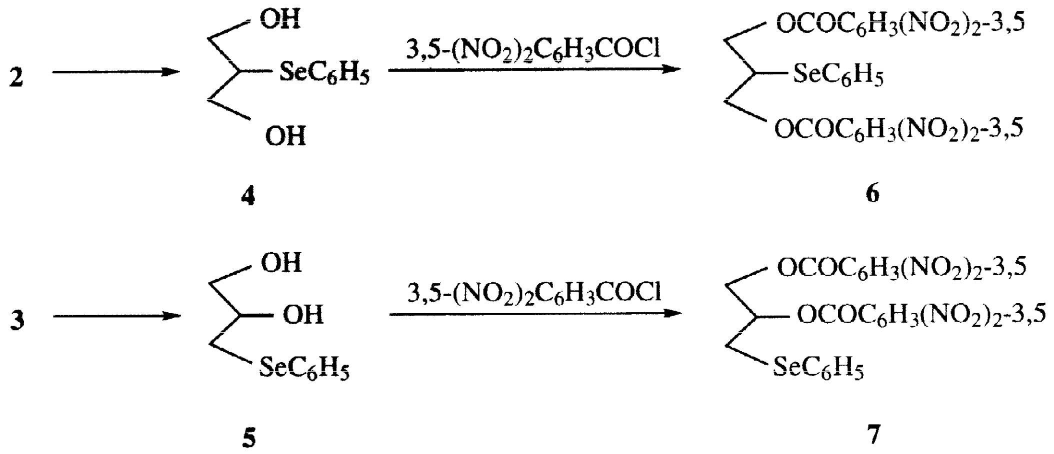


original compound must be **2**. The other compound (**7**) did not give good crystals for X-ray analysis but the hydrolysis product **5** solidified. The elemental analysis and ^{1}H NMR spectra of this solid were consistent with its structure, 3-(phenylseleno)propane-1,2-diol (**5**). [6] The results together with the ^{1}H NMR data indicated that the original product is **3**.

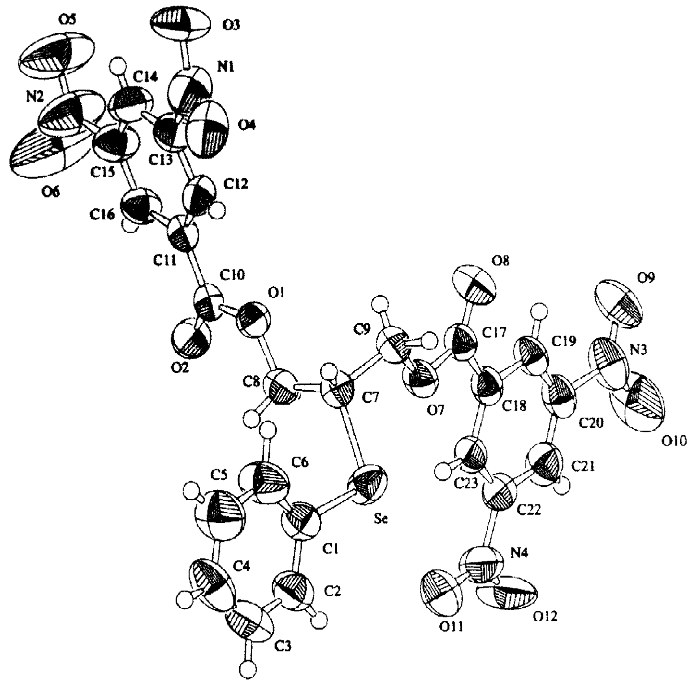
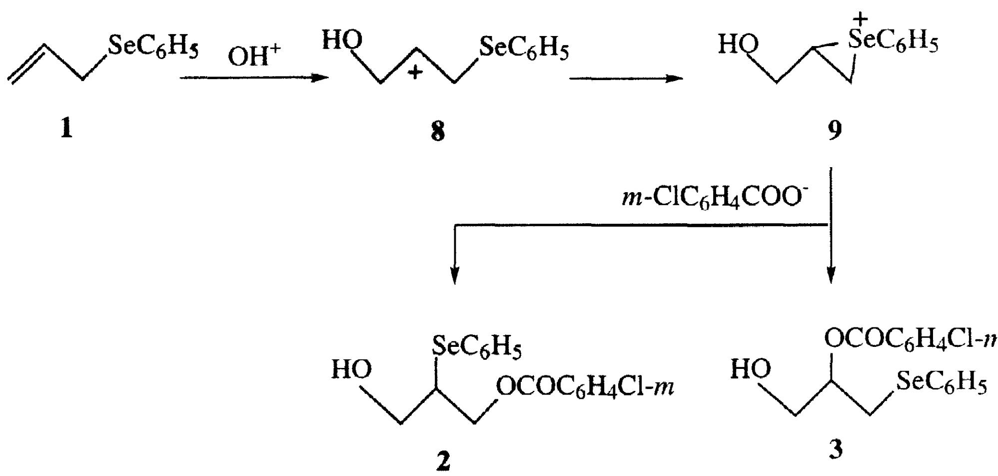


Fig. 1. ORTEP Drawing of 2-(Phenylseleno)propane-1,3-diol Bis(3,5-dinitrobenzoate)

The results were so strikingly different from those of the oxidation of allyl phenyl selenide with hydrogen peroxide that it would be worthwhile to discuss the mechanisms of formation of these compounds. The mechanisms do not involve radical species because the reaction is not retarded by TEMPO. If we assume the intervention of 2-(hydroxymethyl)-1-phenylseleniranium ion (**9**) as an intermediate, all the results are reasonably explained. The simplified mechanism is that the olefinic bond in allyl phenyl selenide is attacked by an OH positive ion to form a cation (**8**), which is stabilized by a selenium atom in the vicinity. [7] Then, the seleniranium ion **9** is formed as an intermediate. When the attack is by a *m*-chlorobenzoate anion, compound **2** is formed when the attack takes place on the methylene side, and compound **3** is formed when the attack takes place on the methine side.



However, this sequence of reactions is unusual because the ionization potential of selenium is much lower than that of the olefinic moiety: [9] The preferential attack of the positive oxygen species on the selenium atom over the olefinic moiety is the natural expectation. Therefore, further evidence to support the postulate that the HO^+ attack on the olefin takes place should be sought.

For this purpose, we carried out ab initio MO calculations on allyl phenyl selenide with the RHF/6-31G* basis set. Results show that there are two stable conformations, extended and folded, the dihedral angles of the $Se\text{-}C_{allyl}$ and C=C bonds being 108.3 and 32.2°, respectively. The extended conformation is more stable than the folded form by 1.50 kcal mol^{-1}. These molecules have a positively charged selenium atom, although it contributes mostly to the HOMO of the molecule. On the other hand, the terminal olefinic CH_2 moieties and the phenyl group are negatively charged, the Mulliken charge of the terminal CH_2 group being -0.026 and -0.007 for the extended and the folded form, respectively. There seem to be electronic interactions between the selenium atom and the olefinic group, the results being consistent with the fact that the allylic selenides undergo facile 1,3-rearrangement. [10]

Thus, the reaction is not HOMO-LUMO controlled, but we believe the interaction of the negative charge of the terminal methylene group with the positively charged OH group in mCPBA is important for the reaction to occur. The reaction may well be a concerted one in which electrons flow from the selenium to the olefinic part and then to the OH^+ ion.

The intervention of the seleniranium ion **9** is also consistent with the product ratio 3:1, because compound **3**, being formed by S_N2 attack of the *m*-chlorobenzoate ion on the secondary alkyl site, is a minor product. At the secondary alkyl site, partial breakage of the Se-C bond probably takes place, because the S_N2 reaction of the secondary alkyl group should be much slower than the primary alkyl group.

Although epoxidation of olefins with peroxycarboxylic acid is generally accepted to proceed via one step, [11] kinetic isotope effects suggest that the transition state of the reaction of olefins with peroxycarboxylic acid is highly unsymmetrical. [12] The present results imply that, at least in the case of allyl phenyl selenide, the addition of OH^+ to the double bond occurs as a distinct step. Although it has been assumed that the oxidations of selenides with hydrogen peroxide and peroxycarboxylic acid proceed via the same mechanisms,

[13] the present results clearly indicate that these can be different from each other. Work to shed light on these problems is in progress.

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References

1. Reich, H. J. "[2,3]Sigmatropic Rearrangements of Organoselenium Compounds" in Liotta, D. ed., "Organoselenium Chemistry", John Wiley, New York (1987).
2. Nishiyama, H.; Itagaki, K.; Sakuta, K.; Itoh, K. *Tetrahedron Lett.*, **22**, 5285 (1981).
3. a) Clive, D. L. J. *Tetrahedron*, **34**, 1049 (1978): b) Duddeck, H., Wagner, P.; Rys, B. *Magn. Reson. Chem.*, **31**, 736 (1993).
4. ^{1}H NMR and IR data were as follows. Compound **2**: ^{1}H NMR (CDCl$_3$) δ = 2.41 (1H, t, J = 5.8 Hz), 3.53-3.61 (1H, m), 3.81-3.88 (2H, m), 4.58 and 4.72 (2H, AB of ABX, J_{AX} = 5.2 Hz, J_{BX} = 7.7 Hz, J_{AB} = 11.6 Hz), 7.28-7.34 (3H, m), 7.38 (1H, t, J = 8.0 Hz), 7.55 (1H, ddd, J = 1.1, 2.2, and 8.0 Hz), 7.61-7.64 (2H, m), 7.89 (1H, ddd, J = 1.4, 1.7, and 7.7 Hz), 7.97 (1H, t, J = 1.7 Hz); IR (neat) 3448, 1722 cm^{-1}. Compound **3**: ^{1}H NMR (CDCl$_3$) δ = 1.91 (1H, br s), 3.24 and 3.29 (2H, AB of ABX, J_{AX} = 6.4 Hz, J_{BX} = 6.5 Hz, J_{AB} = 13.4 Hz), 3.94 (2H, br d), 5.26-5.33 (1H, m), 7.22-7.26 (3H, m), 7.35 (1H, t, J = 8.0 Hz), 7.51-7.57 (3H, m), 7.84 (1H, ddd, J = 1.2, 1.4, and 7.9 Hz), 7.91 (1H, t, J = 1.9 Hz); IR (neat) 3444, 1720 cm^{-1}.
5. Crystallographic data were as follows: empirical formula $C_{25}H_{20}N_4O_{12.5}Se$ [The crystal contained 1/2 mole of tetrahydrofuran for 1 mole of the bis(3,5-dinitrobenzoate).]; formula weight 655.41; crystal dimensions 0.13 × 0.38 × 0.50 mm^3; crystal system triclinic; lattice parameters a = 12.162(1) Å, b = 15.427(2) Å, c = 8.0471(7) Å; α = 102.263(8)°, β = 103.989(7)°, γ = 101.969(8)°, V = 1377.2(3) Å^3; space group $P\bar{1}$, Z = 2; D_{calc} 1.580 g/cm^3; μ(Cu$K\alpha$) 25.07 cm^{-1}; R = 0.056, Rw = 0.086.
6. This compound gave satisfactory analytical results, mp 68 °C. ^{1}H NMR (CDCl$_3$) δ = 2.55 (2H, br s), 2.97 and 3.07 (2H, AB of ABX, J_{AX} = 8.0 Hz, J_{BX} = 4.7 Hz, J_{AB} =12.9 Hz), 3.57 and 3.74 (2H, AB of ABX, J_{AX} = 6.0 Hz, J_{BX} = 3.3 Hz, J_{AB} = 11.2 Hz), 3.75-3.83 (1H, m), 7.26-7.28 (3H, m), 7.52-7.55 (2H, m).
7. Although a referee argued that addition of benzeneselenenic acid to allyl alcohol can explain the results, a reaction of allyl alcohol with 'benzeneselenenic acid' [8] in the presence of *m*-chlorobenzoic acid gave compounds **4** and **5** as overwhelming products under the conditions used.
8. Hori, T.; Sharpless, K. B. *J. Org. Chem.*, **43**, 1689 (1978).
9. Ionization potential of dimethyl selenide is 8.40 eV [Cradock, S.; Whiteford, R. A. *J. Chem. Soc., Dalton Trans. 2*, **68**, 281 (1972)], whereas those of terminal olefins are 9.5–9.7 eV [Turner, D. W. *Adv. Phys. Org. Chem.*, **4**, 31 (1966)].
10. Sharpless, K. B.; Lauer, R. F. *J. Org. Chem.*, **37**, 3073 (1972).
11. Swern, D. "Organic Peroxy Acids as Oxidizing Agents, Epoxidation", Swern, D. ed., "Organic Peroxides", Vol. 2, Chapter V, pp. 355–533, Wiley, New York (1971): Berti, G. *Top. Stereochem.*, **7**, 93 (1973).
12. Hanzlik, R. P.; Shearer, G. O. *J. Am. Chem. Soc.*, **97**, 5231 (1975).
13. Reich, H. J.; Yelm, K. E.; Wollowitz, S. *J. Am. Chem. Soc.*, **105**, 2503 (1983).