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SYNTHESIS AND REARRANGEMENTS OF ortho-SELENONIUM PHENOXIDES

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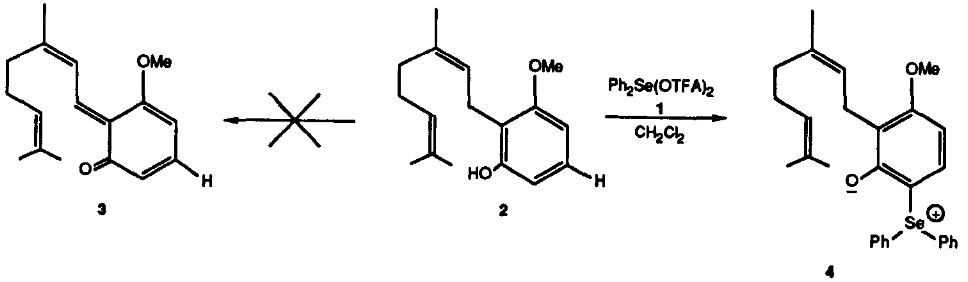
Summary: A new class of selenonium zwitterions is prepared from the ortho-substitution of phenols with diphenylselenium bis(trifluoroacetate) 1. The zwitterions undergo a novel thermal rearrangement to produce diaryl ethers.

During the course of our synthetic efforts to synthesize various tetrahydrocannabinoids *via* intramolecular Diels-Alder reactions of ortho-quinone methides,[1] we attempted the oxidation of the neryl substituted phenol **2** with diphenylselenium bis-trifluoroacetate **1**. We recently introduced selenurane **1** as a mild two-electron oxidant for amines.[2] Instead of the expected phenolic oxidation to a quinone methide **3**, we observed the formation of zwitterion **4**, a member of a new class of selenonium phenoxides. While the sulfonium analogs are well known,[3] only a few reports of the conjugate acids of these selenonium phenoxides are in the literature.[4]

Scheme I

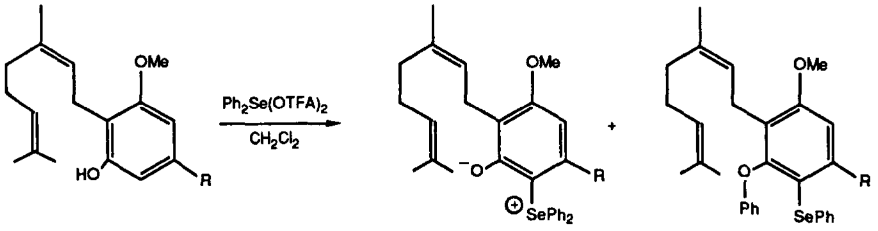


Compound **4** was obtained in 70% yield from the reaction of equimolar amounts of the phenol **2** and diphenylselenium bis-trifluoroacetate (prepared *in situ* from diphenyl sulfoxide and trifluoroacetic anhydride) in methylene chloride at room temperature. After purification by column chromatography, the zwitterion **4** was an off-white solid[5] with characteristic UV behavior for a phenoxide (λ_{max} EtOH, 330 nm; λ_{max} 1N HCl, 255 nm).

The production of a selenonium phenoxide from reagent **1** can easily be envisaged as occurring from an initially formed aryloxy selenurane or directly from a diphenyltrifluoroacetoxy selenonium cation _via_ electrophilic aromatic substitution process. That an initially formed aryloxyselenurane does not fragment to the o-quinone methide and diphenyl selenide may be due to the higher oxidation potential for ortho-substituted phenols relative to their para-isomers.[6]

When a similar reaction was carried out on the 5-n-pentyl analog **5**, a non-polar adduct was isolated in 85% yield with no indication of a zwitterionic product being formed. This new adduct was shown to be the diaryl ether **8** from spectroscopic analyses.[7] The presence of the large n-pentyl substituent clearly diminished the stability of the expected selenonium phenoxide, giving rise to the diaryl ether **8**. In order to test the hypothesis that a selenonium phenoxide is a precursor to the diaryl ether product, the 3-methyl substituted phenol **6** was oxidized with diphenyl selenium bis-trifluoroacetate **1**. In this case, both the selenonium phenoxide **7** (35%) and the diaryl ether **9** (25%) were isolated. The less bulky methyl group permitted the isolation of the zwitterion **7**. That zwitterion **7** is a precursor to diaryl ether **9** can be demonstrated by heating **7** at reflux in DME for 6-7 hours. This thermal rearrangement results in the efficient transfer (95%) of a phenyl group from selenium to the phenoxide oxygen atom.

Scheme II

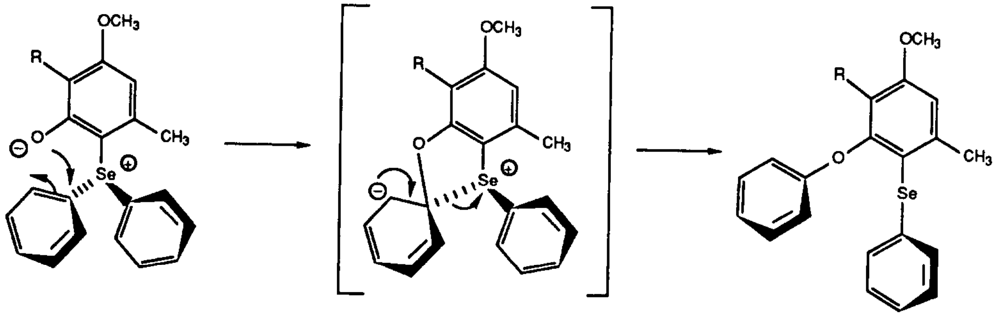


5 R=C_5H_{11}		**8** R=C_5H_{11}
6 R=Me	**7** R=Me	**9** R=Me
2 R=H	**4** R=H	**10** R=H

In a similar manner, zwitterion **4** can be efficiently rearranged to its diaryl ether analog **10**. The intramolecular migration of a phenyl group from a triaryl selenonium cation to an ortho phenoxide is an unprecedented rearrangement to our knowledge. The mechanism for this process is not clear at this time. One possibility for the mechanism includes an intramolecular addition-elimination process as shown below. While an intermolecular version of this process might appear unlikely, the proximity of the oxygen to the selenonium carbon atom and the steric compression of the penta-substituted aromatic ring may render this mechanism plausible. There also exists the possibility of an electron-transfer mechanism involving the phenoxide and the selenonium systems. Similar nucleophilic aromatic substitution reactions have been shown to proceed through a $S_{RN}1$ mechanism.[8]

In summary, the use of a diaryl selenurane reagent such as **1** to produce o-selenonium phenoxides and hence diaryl ethers should provide a new and mild route to highly substituted diaryl ethers. We are currently applying this methodology to the preparation of natural products containing a diaryl ether linkage.

Scheme III



References

1. Marino, J. P.; Dax, S. J. Org. Chem. **1984**, 49, 3671.
2. Marino, J. P.; Larsen, R. D. J. Am. Chem. Soc. **1981**, 103, 4642.
3. Vilsmaier, E.; Sprugel, W. Tetrahedron Lett. **1972**, 625.
4. Funk, H.; Papenroth, W. J. Prakt. Chem. **1960**, 11, 191.
5. d.p. 124-126. All new compounds gave correct elemental analyses.
6. We have found that reagent **1** does efficiently oxidize 2,4,6-trisubstituted phenols to p-quinone methides under the same reaction conditions; unpublished results with C. Deering.
7. Compound **8** is an oil with a UV λ_{max} (EtOH) @ 255 nm which was unaffected by acid or base. IR ($CHCl_3$): 3070-2800 cm^{-1} (s), 1595 cm^{-1} (s), 1580 cm^{-1} (m), 1560 cm^{-1} (m). NMR ($CDCl_3$, 360 MHz, ppm): 0.84 (3H), 1.24-1.28 (4H), 1.52 (2H), 1.53, 1.55 (6H), 1.63 (3H), 1.92-1.97 (4H), 2.8 (2H), 3.2 (2H), 3.87 (3H), 5.04-5.12 (2H), 6.61 (2H), 6.74 (1H), 6.85-6.89 (1H), 7.08 (6H), 7.12-7.17 (1H).
8. Bunnett, J. F. Acc. Chem. Res. **1978**, 11, 413.

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