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Oxygen Induced Free-Radical Addition of Benzeneselenol to Allenes

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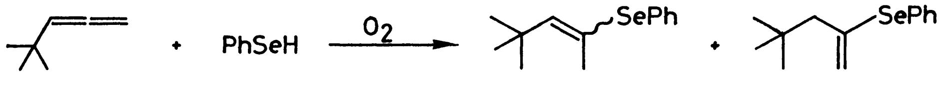
The addition of benzeneselenol to mono- and disubstituted allenes proceeded in the presence of oxygen to give vinyl selenides in excellent yields. This reaction is likely to involve a radical chain process initiated by oxygen.

Vinyl selenides have become widely employed in organic synthesis and various methods have been devised for their preparation.1) Their sulfur analogues, vinyl sulfides, are also useful in synthesis.2) While one of the simplest access to vinyl sulfides may be the addition of thiols to allenes,3) no corresponding reaction of selenols has been reported. We have studied the reaction of benzeneselenol (**1**) with allenes and, interestingly, have found that **1** adds very smoothly to allenes just on mixing. As will be described below, this apparently spontaneous addition seems to be initiated with oxygen in the reaction mixture and governed by a free radical mechanism. Some of the results would be of preparative use.

The reaction was performed simply by adding **1** (3 mmol) to a benzene-d_6 (0.3 mL) solution of allene **2** (1 mmol) at 25 °C in a sealed NMR tube filled with oxygen and was monitored by NMR.

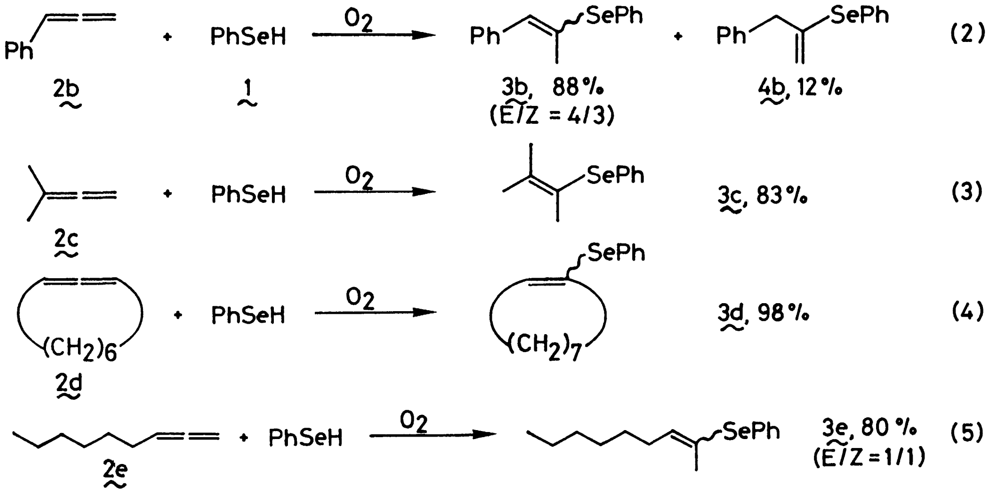
In the case of t-butylallene (**2a**), no reaction occurred without oxygen (25 °C, 24 h). However, in the presence of oxygen, the addition proceeded gradually, and vinyl selenides **3a** and **4a** were formed in a 9 : 1 ratio in 48 h (Eq. 1).4) The quantitative analysis and structural assignment of these products were made on the basis of the spectroscopic data. In the ^{1}H NMR spectra, **4a** displayed the characteristic signals due to two olefinic protons at δ 5.12 and δ 5.33, whereas **3a** showed absorptions at δ 6.16 for the E isomer and δ 5.87 for the Z isomer. No 2:1 adduct was detected by NMR.



2a 1 3a, 70% (E/Z=2/1) 4a, 8% (1)

It is known that **1** reacts with oxygen to yield diphenyl diselenide,5) probably via a phenylseleno radical. Since the addition proceeded only when oxygen was present, it might involve the radical chain process initiated by oxygen. The addition of phenylthio radical to the allene **2a** is reported to occur at the central and terminal carbon atoms in a 75:25 ratio,3) whereas the addition of phenylseleno radical took place selectively at the central carbon leading to a stable allyl radical.

In the cases of phenylallene (**2b**), 1,1-dimethylallene (**2c**), and 1,2-cyclononadiene (**2d**), the reaction was exothermic and complete within a few minutes to form vinyl selenides **3b-d** and **4b**. Hexylallene (**2e**) gave 80% of vinyl selenides **3e** in 48 h.



In general, reaction between a carbon radical and oxygen is very fast. However, such reaction is not observed at all in the present reaction which does involve carbon radicals as the intermediate. This fact may be due to an extraordinarily high hydrogen transfer ability of 1.[6)]

The addition of benzeneselenol to acetylenes has been known.[7)] We suggest that this reaction may well involve an oxygen-induced free radical process. Many other known reactions of 1[8)] would be rationalized in a similar way. Studies along with this line are now in progress.

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References

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