

One Step Vinylic Chlorination with Benzeneseleninyl Chloride

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The reaction of benzeneseleninyl chloride with olefins in the presence of aluminum chloride or ruthenium(II) phosphine complex under mild conditions was found to give α -chloro-olefins in one step.

In recent years the application of organic selenium reagents became a very powerful tool in organic synthesis.¹⁾ Of particular importance is the phenyl-seleno group owing to its rather fertile and easily manipulated nature. A carbon-carbon double bond is easily formed by the oxidation of selenide to selenoxide and the subsequent syn-elimination of benzeneselenenic acid with β -hydrogen. We found that the reaction of benzeneseleninyl chloride (1) with olefins in the presence of a catalyst in dichloromethane under mild conditions afforded chloro-olefins. The results will be described in this communication.

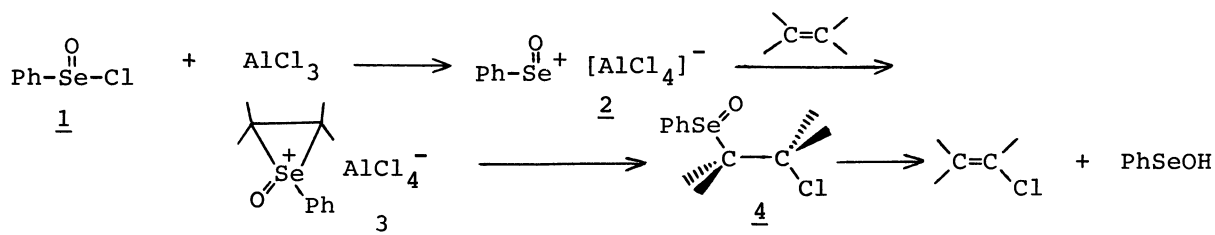
In a typical example, to a solution of benzeneseleninyl chloride,²⁾ prepared by ozonization of 2.0 mmol of benzeneselenenyl chloride in 60 ml of dichloromethane, were added 2.0 mmol of 1,1-diphenylethylene and 2.0 mmol of aluminum chloride, and the mixture was stirred at room temperature for 2 h. The reaction mixture was colored to red then to brown. GC analysis showed that starting 1,1-diphenylethylene was completely consumed. Water was added to the mixture, and the organic layer was washed three times with water and dried over anhydrous magnesium sulfate. After evaporation of the solvent under reduced pressure, the residue was distilled by Kugelrohr to give a colorless oil (289 mg, 67% yield; bp 118 °C/0.5 Torr) which was identified as 2-chloro-1,1-diphenylethylene by its IR, ¹H NMR, and MS spectral data, and the yield determined by GC was 94%. The reaction proceeded very slowly when the reaction was carried out without catalyst, and 2-chloro-1,1-diphenylethylene was obtained in 43% yield after 142 h at 40 °C. Similarly, triphenylethylene was treated with benzeneseleninyl chloride and aluminum chloride in dichloromethane to give chlorotriphenylethylene in quantitative yield.



R = H or Ph

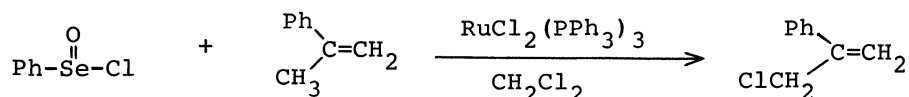
The reaction is accounted for by the activation of benzeneseleninyl chloride by the catalyst giving benzeneseleninyl cation intermediate (2) which adds to olefins electrophilically affords epioxoselenonium ion³⁾ intermediate (3). The

chloride ion attacks the α -carbon to give a ring opening adduct (4) which readily eliminates benzeneselenenic acid to give chloro-olefin as shown below.

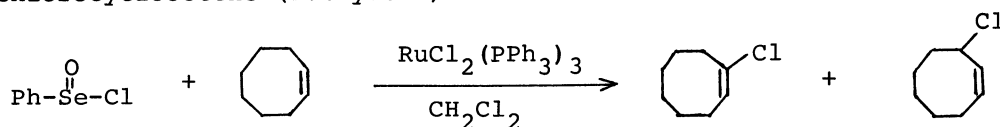


Direct replacement of the vinylic hydrogen by chlorine atom is very difficult either by ionic substitution or radical chlorination. As shown above, benzeneselenenyl chloride is an excellent reagent to introduce chlorine atom on olefinic carbon in one step.

While the aluminum chloride did not catalyze the reaction of benzeneselenenyl chloride with α -methylstyrene, dichlorotris(triphenylphosphine)ruthenium(II) catalyzed the reaction. In this case, the expected 1-chloro-2-phenylpropene was not formed but isomeric 3-chloro-2-phenylpropene was obtained in 43% yield.



The reaction of benzeneselenenyl chloride with cyclooctene in the presence of dichlorotris(triphenylphosphine)ruthenium(II) gave 1-chlorocyclooctene (19% yield) and 3-chlorocyclooctene (27% yield).



The ruthenium(II) catalyzed reaction is accounted for by a redox-transfer radical mechanism forming benzeneselenenyl radical and Ru(III)Cl intermediate, which react with olefins to give adduct 4.⁴⁾ The benzeneselenenyl group is considered to be eliminated with either of two vicinal hydrogens from the adduct 4.

Further studies on the scope and limitation of the benzeneselenenyl chloride as vinylic chlorination reagent are now in progress.

References

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- 3) Oxoselenonium and epioxoselenonium salts are hitherto unknown. However, we have recently succeeded to prepare several triaryloxoselenonium salts: M. Kobayashi and T. Mihoya, *Chem. Lett.*, **1986**, 809.
- 4) The reactions of sulfonyl chlorides with olefins catalyzed by Ru(II) complex involving radical mechanism to give 1:1 adducts have been reported: N. Kamigata, H. Sawada, N. Suzuki, and M. Kobayashi, *Phosphorus and Sulfur*, **19**, 199 (1984).

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