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[Lab. of Pharm.

First Isolation of Selenabenzenes Stabilized by Two Electron-withdrawing Groups at the 2- and 6-Positions.

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Selenabenzenes with two electron-withdrawing groups at 2,6-positions were synthesized as stable compounds at room temperature via processes of ring closure, C=C bond construction, alkylation and deprotonation. Their structures were characterized by the ¹H-, ¹³C- and ⁷⁷Se-NMR and IR spectra. Two electron-withdrawing groups delocalize the negative charge and the difference in the chemical shifts between C(3,5) and C(4) is attributable to the difference in the electron density at the 3,5- and 4-positions. The selenabenzenes underwent the thermal rearrangement giving 2- and 4-methylselenines and the oxygenation reaction giving dienone and selenin-4-one.

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A Novel Preparation of Chiral (*Z*)-*O*-Alkyl Enol Ethers From Alkenylselenonium Salts.

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The reaction of diphenylalkynylselenonium salt with benzyl alcohol and sodium benzenesulfinate in CH₃CN proceeded within 30 minutes to give β-sulfonyl enol ether in high yield (90%). In the cases of secondary alcohols, however, their bulkiness decreased the yields of the enol ethers and in particular, the reaction with sterically hindered secondary cyclic alcohol, (-)-menthol did not produce an enol ether. The reaction of diphenylalkenylselenonium salt with (+)-1-phenylethanol as an acyclic secondary alcohol was conducted in the presence of NaH at -30°C only for 30 minutes and gave an *O*-alkyl enol ether in high yield (91%). The reaction of dimethylalkenylselenonium salt with lithium menthoxide, prepared from PhLi and menthol, in THF at -78°C successfully afforded the desired product in 80% yield.

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[Lab. of Pharm. Chemistry]

**Reactions of Alkynylselenonium Salts with Tetrabutylammonium Halides:
Apparent Umpolung of Alkynyl Moiety.**

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The reactions of diphenyl(phenylethynyl)selenonium triflate with *n*-Bu₄NI in CH₂Cl₂ gave phenylethynyl iodide (74%) and diphenyl selenide (82%). *n*-Bu₄NBr and *n*-Bu₄NCl were less reactive than *n*-Bu₄NI. Phenylethynyl bromide was obtained in only 36% yield. Alkynyl chloride was not obtained from the reaction of the alkynylselenonium salt with *n*-Bu₄NCl but 2-chloroacetophenone derivative were given in low yield. In contrast, the reaction with *n*-Bu₄NF in CH₂Cl₂ gave diphenyl selenoxide in good yield. The counterpart, phenylacetylene, was analyzed directly by HPLC of the reaction mixture in 88% yield. Diphenyl selenide was not converted into diphenyl selenoxide by treatment with *n*-Bu₄NF. Thus, the alkynyl moiety of the selenonium salt acted as the alkynyl cation or the acetylide ion depending upon the kind of halide ion and we could find apparent umpolung of the alkynyl moiety.

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The First Example of Formation of the Benzyne Intermediate from the Reactions of Selenonium Salts with Phenyllithium.

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We examined the reactions of diphenyl(phenylethynyl)selenonium triflate with phenyllithium in THF in various conditions. These reactions revealed four interesting result: (1) 1,4-diphenylbutadiyne was obtained in all cases; (2) 1-(*o*-biphenyl)-2-phenylethyne was given in low yield; (3) when 0.5 equivalent of phenyllithium was used, the selenonium salt as starting material was not recovered but triphenylselenonium triflate was obtained; (4) when the quantity of phenyllithium was increased, the yields of 1,4-diphenylbutadiyne and 1-(*o*-biphenyl)-2-phenylethyne were decreased and phenylethyne was increased. On the basis of these results, we have shown that the first step of the reaction of the selenonium salt with phenyllithium quickly caused the ligand exchange reaction to form triphenylselenonium triflate and phenylethynyllithium, followed by the evolution of benzyne.