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Samarium(II) Di-iodide Induced Synthesis of Allylic Phenyl Selenides from Allylic Acetates and Diphenyl Diselenide in the Presence of Palladium Catalyst

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Allylic phenyl selenides are prepared efficiently from the reaction of allylic acetates and diphenyl diselenide induced by samarium(II) diiodide in the presence of a palladium catalyst under mild conditions.

Allylic selenides have been recognized as useful synthons of allylic anion stabilized by seleno group, and they are regioselectively α-alkylated.1) The facile oxidative conversion of allylic selenides to alcohols accompanied by a [2.3]sigmatropic rearrangement is a useful synthetic transformation.2) A nucleophilic substitution of allylic halides with phenylseleno anion has been accepted as a general method for preparation of allylic selenides.3) More easily accessible allylic acetates are another candidates for starting organic compounds. However, the direct displacement of allylic acetates with phenylseleno anion does not appear to be efficient. 1a) In the single example reported, geranyl acetate is converted into the corresponding selenide at reflux in ethanol for 24 h, but the yield is not satisfactory.4) Phenylselenotrimethylsilane is an efficient reagent for the direct preparation of allylic selenides from allylic acetates in the presence of a catalytic amount of zinc iodide.5)

On the other hand, it has been reported that generation of "allyl anion" from allyl acetate *via* polarity inversion of π-allyl palladium complex promoted by samarium(II) diiodide and its trapping with some electrophiles. 6) We now found that this polarity inversion of π-allyl palladium complex lead to an efficeint method for preparation of allylic selenides from easily accessible diphenyl diselenide and allylic acetates, although a selenium compound is generally recognized as a catalyst poison.

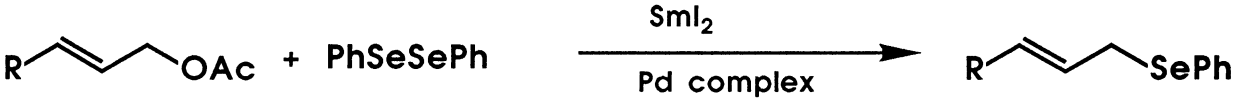
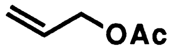
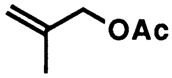
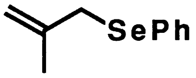
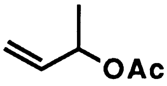
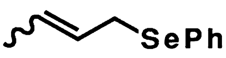
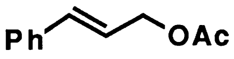
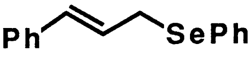
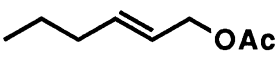
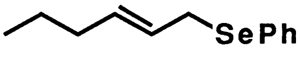
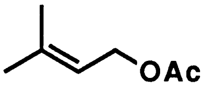
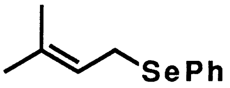
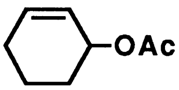
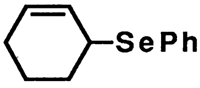


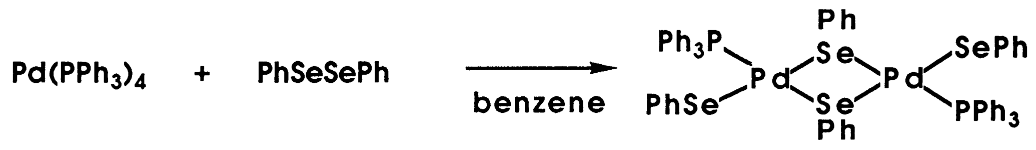
Table 1. Samarium(II) Diiodide Induced Synthesis of Allylic Selenides Catalyzed by Palladium Complex [a)]

Run	Allylic acetate	Product	Yield/% [b)]
1[c)]			82
2[c)]			84
3			70 (E/Z=2.17/1) [d)]
4			75 (E/Z=1.94/1) [d)]
5			47
6			60
7			64
8			81

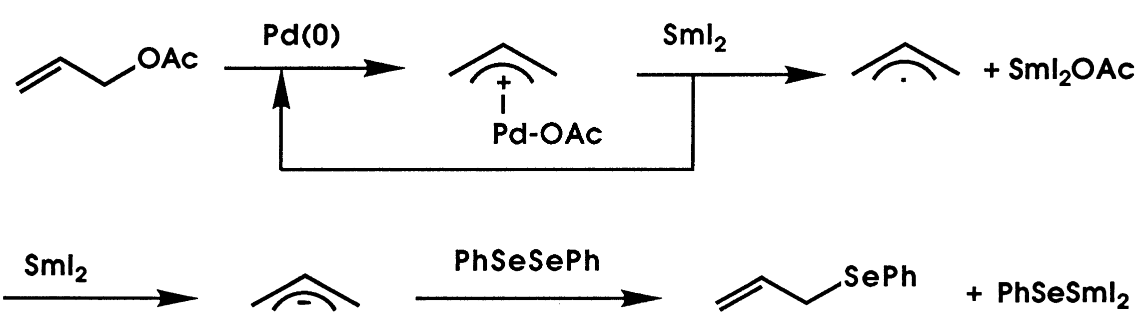
a) Allylic acetate (1.0 mmol), diphenyl diselenide (1.0 mmol), samarium diiodide (2.5 mmol), palladium chloride (0.05 mmol), triphenylphosphine (0.2 mmol), and THF (10 ml); 25 °C, 10-15 h. b) Yields are calculated based on allylic acetate and deterimed by GLC. c) Reaction time was 2 h. d) Isomer ratio was determined by GLC.

The results from the reaction of various allylic acetates are shown in the Table. Each reaction was carried out using 1.0 mmol each of allylic acetate, diphenyl diselenide, 2.5 mmol of samarium(II) diiodide, and a catalytic amount of palladium chloride (0.05 mmol) and triphenylphosphine (0.2 mmol) 7) in tetrahydrofuran (THF) (10 ml) under nitrogen at room temperature.8) The end of the reaction was confirmed by complete consume of a starting allylic acetate with GLC analyses. Allyl and methallyl acetate reacted smoothly with diphenyl diselenide to give the corresponding allylic selenide in good yields in a short time (2 h) (runs 1-2). Other substituted allylic acetates, however, required a longer reaction time (10-15 h) to complete the reaction. In any cases, the reaction proceeded at room temperature and the yields were satisfactory. Crotyl and 1-buten-3-yl acetate gave the same selenide (crotyl phenyl selenide), without contamination of the isomer (runs 3-4).9) The reaction did not proceed without either samarium(II) diiodide or a palladium catalyst.

It is surprising that a palladium complex worked effectively as a catalyst in the reaction, although selenium compounds have been recognized as a catalyst poison. It has been reported that palladium complexes of organoseleno ligands such as complex (A) are formed from palladium phosphine complexes and organoselenium compounds.10) To examine the possible catalytic activity of the complex, we prepared it from $Pd(PPh_3)_4$ and diphenyl diselenide in benzene, but it gave allylic selenide only in a poor yield (<8%) under the conditions.11) This result may suggest that the complex (A) is not involved in the reaction. The mechanism and stoicheometry of the reaction is not yet clear, but the following possible mechanism is tentatively proposed. Allylic radical and anion species are involved as the result of the polarity inversion of π-allyl palladium complex by samarium(II) diiodide reduction. 6) Further studies are now in progress.



(A)



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2) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **94**, 7154 (1972) ; **95**, 2697 (1973); H. J. Reich, *J. Org. Chem.*, **40**, 2570 (1975).

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4) K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patric, S. P. Singer, and M. W. Young, *Chemica Scripta*, **8A**, 9 (1975).

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6) T. Tabuchi, J. Inanaga, and M. Yamaguchi, *Tetrahedron Lett.*, **27**, 601, 1195, 5273 (1986).

7) $Pd(PPh_3)_4$ and $NiCl_2(PPh_3)_2$ can be replaced by $PdCl_2$ and PPh_3.

8) Typical experimental procedure is as follows. Deep green THF(5 ml) solution of samarium(II) diiodide was prepared from samarium powder (0.38 g, 2.5 mmol) and methlene diiodide (0.67 g, 2.5 mmol). $PdCl_2$ (9 mg, 0.05 mmol) and PPh_3 (52 mg, 0.2 mmol) were added to the solution and the mixture was stirred for 10 min at room temperature. To the resulting solution was added a mixture of diphenyl diselenide (0.31 g, 1 mmol) and allyl acetate (0.10 g, 1 mmol) in THF (5 ml) and the solution was stirred at room temperature for 2 h. After usual workup, GLC analysis of the extract revealed the presence of allyl phenly selenide. Yield was determined by GLC using diphenyl as an internal standard.

9) Similar rearrangement is observed in the reaction of the allylic acetates with phenylselenotrimethylsilane. (5)

10) H. J. Gysling, " The Chemistry of Organic Selenium and Tellurium Compounds ", ed by S. Patai and Z. Rappoport, John Wiley & Sons Ltd., Chichestor (1986),Vol. 1, Chap. 18, pp. 679-855.

11) It has recently been reported that sulfur analog of complex (**A**) works as catalyst for addition reaction of diphenyl disulfide to acetylene. H. Kuniyasu, A. Ogawa, S. Miyazaki, I. Ryu, N. Kambe, and N. Sonoda, 36th Symposium on Organometallic Chemistry, Japan, Abstract PB109, 277, 1989, Tokyo.

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