

Samarium(II) Diiodide Induced Polarity Inversion of π -Allyl Palladium Complexes: The Formation of Allylic Selenides

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Abstract: Allylic acetates were reduced with Pd(0)-SmI₂ in the presence of ArSeBr to form corresponding allylic selenides in good yields.

Keywords: Allyl acetates, allylic selenides, arylselenenyl bromides, palladium complexes, polarity inversion.

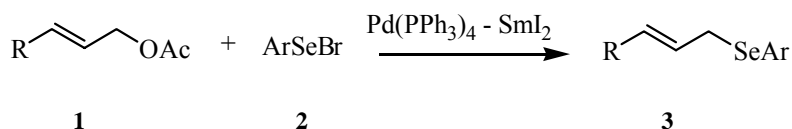
As a versatile one-electron transfer reducing and coupling agent, samarium diiodide has been extensively used in organic synthesis in last decade. It has been reported that electrophilic π -allyl palladium complexes could undergo polarity inversion to nucleophilic species with the aid of SmI₂, and could trap some electrophiles¹. It is well known that allylic selenides are rather important intermediates in organic synthesis. They have been recognized as useful synthons of allylic anion stabilized by seleno group, and they are regioselectively α -alkylated^{2,3}. In literature a variety of synthetic methods for allylic selenides have been reported such as nucleophilic substitution of allylic halides with phenylseleno anion^{4,5}. However, those methods have the disadvantages of being in low yields or long reaction time.

We found that the SmI₂ induced polarity inversion of π -allyl palladium complex could be an efficient method for preparation of allylic selenides from electrophilic arylselenenyl bromides and allylic acetates (**Scheme 1**). In this reaction, we added arylselenenyl bromides **2** to the mixed solution of SmI₂, Pd(PPh₃)₄ and allylic acetates **1** in THF, corresponding allylic selenides **3** were formed after being stirred for 4 h at room temperature in good yields. The results are listed in **Table 1**. The structure of compounds **3a-3e** was confirmed by IR and ¹H NMR⁶. The mechanism of reaction was proposed as follows: Allyl acetate reacted with Pd(PPh₃)₄ to form π -allyl palladium complex. The complex was converted to allyl anion *via* reduction with SmI₂. Then the allyl anion trapped ArSeBr to yield allylic selenides.

General procedure: A solution of SmI₂ (5 mmol) in THF (30 mL) was added to allyl acetate **1** (2 mmol) in anhydrous THF (3 mL), followed by Pd(PPh₃)₄ (0.05 mmol) under

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Scheme 1



the nitrogen atmosphere. The mixture was stirred at room temperature for 0.5 h. Then phenylselenenyl bromide **2** (2.2 mmol) in THF (10 mL) was added dropwise to it. The resulting mixture was continued to be stirred at room temperature for 4 h (the reaction was monitored by TLC). After evaporation of THF, the crude product was diluted with ethyl ether (30 mL), washed with saturated solution of NaCl (3×30 mL), dried over Na₂SO₄ and concentrated. The crude product was purified by TLC on silica gel to form corresponding allylic selenide **3** in 58% yield.

Table 1 SmI₂ induced synthesis of allylic selenides catalyzed by palladium complexes

Entry	R	Ar	Time (h)	Isolated yield ^a (%)	mp (°C)	Lit. mp (°C)
3a	H	C ₆ H ₅	4.5	58	oil	oil
3b	H	4-CH ₃ C ₆ H ₄	4.5	53	oil	oil
3c	H	4-CH ₃ OC ₆ H ₄	4.5	51	oil	oil
3d	C ₆ H ₅	C ₆ H ₅	5	49	62-63	64-65 ⁷
3e	C ₆ H ₅	4-CH ₃ C ₆ H ₄	5	47	53-54	54.5-55.5 ⁷

In summary, a new route for prepare allylic selenides has been provided utilizing samarium diiodide induced polarity inversion of π -allyl palladium complexes under mild and neutral condition.

References and Notes

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- ¹H NMR (CDCl₃, δ_{H} ppm):
3a: 3.20-3.33 (d, 2H, *J*=7Hz), 4.63-4.80 (m, 2H), 5.43-6.10 (m, 1H), 6.93-7.33 (m, 5H). **3b**: 2.17 (s, 3H), 3.17-3.30 (d, 2H, *J*=7Hz), 4.56-4.78 (m, 2H), 5.23-6.03 (m, 1H), 6.70-7.18 (m, 4H). **3c**: 3.63 (s, 3H), 3.17-3.28 (d, 2H, *J*=6Hz), 4.61-4.76 (m, 2H), 5.40-5.96 (m, 1H), 6.47-7.30 (m, 4H). **3d**: 3.43-3.53 (m, 2H), 5.83-6.12 (m, 2H), 7.13-7.33 (m, 5H). **3e**: 2.23 (s, 3H), 3.43-3.57 (m, 2H), 5.97-6.23 (m, 2H), 6.73-7.37 (m, 4H).
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