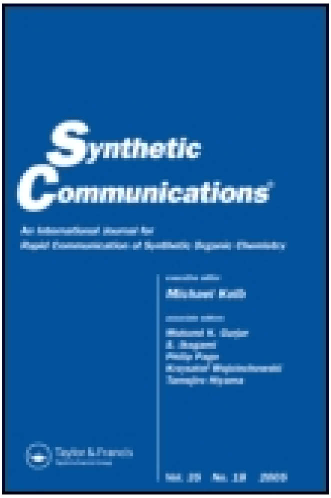

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# A New Method for the Synthesis of Allyl Arylselenides via the Reaction of the Zinc Allyl Selenoates with Diaryliodonium Salts

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# A NEW METHOD FOR THE SYNTHESIS OF ALLYL ARYLSELENIDES *VIA* THE REACTION OF THE ZINC ALLYL SELENOATES WITH DIARYLIODONIUM SALTS

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**Abstract:** The insertion of elemental selenium into the Zn-C bond of allylzinc bromide in THF leads to the corresponding zinc allyl selenoate. It reacts with diaryliodonium salts in THF-HMPA to afford the allyl arylselenides in high yields.

Allyl selenides are important intermediates in organic synthesis. For example they can form allyl anion stabilized by seleno group and further can be α-alkylated regioselectively[1]. They also can carry out [2, 3] sigmatropic rearrangements to give allyl alcohols[2]. Preparation of allyl selenides usually uses diselenides as starting materials. To our knowledge, diaryl diselenides can react with allyl acetates or allyl bromide promoted by palladium[3], indium or samarium[4]. In additions α-seleno ketones also can be converted into allyl selenides via severalsteps[5]. But some of these methods have certain disadvantages such as the

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necessity of using expensive transition metals or troublesome laborious manipulations. Now we report a new convenient method for the preparation of allyl arylselenides via the reaction of the zinc allyl selenoates with diaryliodonium salts.

According to the literature, transition metal selenoates or selenium complexes all have good nucleophilicity in aprotic solvents. They can be reacted with various electrophiles under mild conditions[6~10]. A convenient method for their preparation is via the insertion of selenium into transition metal-carbon bonds. The insertion of selenium into the M-C (M=Zr, Hf) bond has been reported[6~7]. Zinc is a very abundant, relatively inexpensive and generally nontoxic element. Moreover, organozinc compounds are readily prepared by oxidative addition of zinc to alkyl, allyl or benzyl halides, or by transmetallation reactions. This led us to study the insertion of selenium into the zinc carbon bond. We investigated the reaction of selenium with allylzinc bromide. We found that the reaction could be smoothly carried out in THF and gave the corresponding zinc allyl seleoates. In order to prepare the allyl arylselenides, we investigated the reaction of the zinc allyl selenoates with some arylating reagents. The results showed that the zinc allyl selenoates do not react with haloarenes, even the active p-chloro nitrobenzene. Diaryliodonium salts are efficient electrophilic arylating reagents. We further investigated the reactions of zinc allyl selenoate with diaryliodonium salts. The experimental results showed that the reaction could be carried out in THF-HMPA and gave allyl arylselenides in high yields (Table 1).

$$\mathrm{RCH{=}CH\text{-}CH_2Br} \xrightarrow[\text{THF } 0\sim10^\circ\text{C}]{\text{Zn}} \mathrm{RCH{=}CH\text{-}CH_2ZnBr} \xrightarrow{\text{Se}} \mathrm{RCH{=}CH\text{-}CH_2SeZnBr}$$

$$\xrightarrow[\text{THF-HMPA } 40^\circ\text{C}]{\mathrm{ArI^{+}ArX^{-}}} \underset{\textbf{1a-h}}{\mathrm{RCH{=}CH\text{-}CH_2SeAr}}$$

We examined the influence of solvents upon the reaction. In THF-HMPA (2:1) the yield was best (Table 1).

The present method provides a new path for the synthesis of allyl selenide. Moreover, it has advantages of available starting materials and simple manipulation.

## Experimental

$^1$HNMR spectra were recorded on PMX-60 spectrometer. IR spectra were determined on PE-683 spectrophotometer. Tetrahydrofuran was distilled from sodium benzophone. Commercial HMPA was dried over calcium hydride, distilled in vacuo and stored over 4A molecular sieves. All reactions were carried out under nitrogen.

A representative procedure for the synthesis of allyl arylselenides is as follows: the activated zinc power 0.130g (2.0mmol) reacted with allyl bromide (2.0mmol) in 10ml THF at 0~10 ℃. When the zinc power had dissolved, dried selenium (2.0mmol) was added portionwise to the solution. Which was stirred the mixture at r.t. for 1h then refluxed till the selenium disappeared. To the solution was then added the diaryliodonium salt ( 2.0mmol ) and HMPA (5ml) and the mixture was

Table 1 Synthesis of Allyl Arylselenides.

| Entry | Product | Solvents(ml) | Yield* |
|---|---|---|---|
| **1a** | $PhSeCH_2CH=CH_2$ | THF(15) | 40 |
| **1b** | $PhSeCH_2CH=CH_2$ | THF-DMF (10/5) | 58 |
| **1c** | $PhSeCH_2CH=CH_2$ | THF-HMPA (10/5) | 70 |
| **1d** | $p\text{-}CH_3C_6H_4SeCH_2CH=CH_2$ | THF-HMPA (10/5) | 65 |
| **1e** | $p\text{-}ClC_6H_4SeCH_2CH=CH_2$ | THF-HMPA (10/5) | 78 |
| **1f** | $p\text{-}CH_3OC_6H_4SeCH_2CH=CH_2$ | THF-HMPA (10/5) | 75 |
| **1g** |  SePh | THF-HMPA (10/5) | 70 |
| **1h** |  $SeC_6H_4CH_3\text{-}p$ | THF-HMPA (10/5) | 65 |

isolated yield. reaction temperature: 40 ℃, time: 12h.

stirred for 12h at 40 ℃. It was then diluted with dilute aqueous HCl (20ml), and the aqueous layer was extracted with ether (3 × 20ml). The combined organic phase was washed with a saturated aqueous $Na_2CO_3$ solution and brine and dried ($MgSO_4$) and the solvent was evaporated. The residue was subjected to preparative TLC on silica gel using light petroleum-ether as eluent (30:1).

**1a** : IR ($cm^{-1}$) 3010, 2995, 1640, 1585, 1475, 1070. $^1$HNMR (δ,ppm) 3.31(d,2H), 4.46(-4.98(m,2H), 5.46-6.15(m,1H), 7.06-7.56(m,5H).

**1d** : IR ($cm^{-1}$) 3030, 2995, 1640, 1600, 1495, 1130. $^1$HNMR (δ,ppm) 2.20(s,3H), 3.35(d,2H,J=7.2Hz), 4.67-4.93(m,2H), 5.47-6.17(m,1H), 7.04-7.49(m,4H).

**1f** IR ($cm^{-1}$) 3010, 2985, 1650, 1600, 1495, 910. $^1$HNMR (δ,ppm) 3.28(d,2H), 3.66(s,3H), 4.50-4.80(m,2H), 5.40-6.02(m,1H), 6.58(d,2H,J=8Hz), 7.27(d,2H, J=8Hz).

**1g** : IR ($cm^{-1}$) 2980, 1650, 1590, 1485, 1075, 685. $^1$HNMR (δ,ppm) 1.59-1.93(m,6H), 3.82(m,1H), 5.30-5.91(m,2H),7.06-7.56(m,5H).

**1h** : IR ($cm^{-1}$) 3050, 2980, 1655, 1480, 1260, 865. $^1$HNMR (δ,ppm) 1.53-2.06(m,6H), 3.75(m,1H),5.47-5.83(m,2H),7.00-7.43(m,4H).

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