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# Stereoselective Synthesis of (E,E)-1-Arylselenobutadienes by Cross-Coupling Reactions in the Presence of Palladium Catalyst

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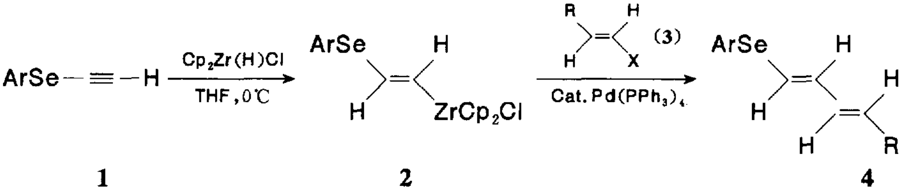
***Abstract*:** Hydrozirconation of arylselenoethynes **1** gives selenium-containing zirconium(Ⅳ) complexes **2**, which are cross-coupled with alkenyl halides in the presence of $Pd(PPh_3)_4$ to afford (E,E)-1-arylselenobutadienes **4** in high yields.

The stereocontrolled synthesis of conjugated dienes is of considerable interest in organic synthesis since such dienes are often encountered in natural compounds, such as Achillea amide[1], and are also valuable intermediates in the synthesis of more complex targets via Diels-Alder reaction[2].

In literature, we found the stereoselective synthesis of (E, E)-1-trimethylsilylbutadienes[3,4], (E,E)-1-phenylthiobutadienes[5]. However, there are few reports on the synthesis of (E,E)-1-arylselenobutadienes[6].

Hydrozirconation[7] can tolerate certain ether functionalities, such as OEt and OTHP group[8], and the (E)-1-alkenylzirconium compounds thus obtained can react with alkenyl halides in the presence of catalytic amount of $Pd(PPh_3)_4$ or $Ni(PPh_3)_4$ to form 1,3-butadienes containing such functional groups[8,9].

We tried reacting arylselenoethynes **1**[10] with $Cp_2Zr(H)Cl$ and found that selenium-containing zirconium (Ⅳ) complexes **2** were formed. Cross-coupling reaction of complexes **2** with alkenyl halides **3** in the presence of $Pd(PPh_3)_4$ afforded (E,E)-1-arylselenobutadienes **4** stereoselectively in high yields. We found that the optimum molar ratio of $Cp_2Zr(H)Cl$ to compound **1** was 1 : 1. The experimental results are summarized in Table 1.



**Scheme 1**

**Table 1** Synthesis of (E,E)-1-Arylselenobutadienes **4a-d**

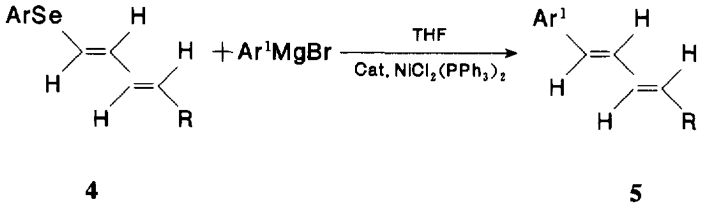
| Ar in **1** | **3** | | Product **4** | Yield(%)[a] |
|---|---|---|---|---|
| | R | X | | |
| Ph | Ph | Br | **4a** | 82 |
| Ph | Ph | I | **4a** | 77 |
| Ph | $CH_3OCH_2$ | Br | **4b** | 86 |
| 4-$MeC_6H_4$ | Ph | Br | **4c** | 80 |
| 4-$MeC_6H_4$ | Ph | I | 4c | 79 |
| 4-$MeC_6H_4$ | $CH_3OCH_2$ | Br | **4d** | 88 |

a. isolated yield b. The configuration of double bonds were determined by $^1$HNMR[11,12].

The alkenyl halides were prepared by hydrozirconation of 1-alkynes followed by trapping with electrophilic halogenation ($I_2$ or N-bromosuccinimide)[13].

The major advantages of this coupling reaction are the preparation convenience of (E)-2-arylselenoalkenyl zirconium complexes **2** via hydrozirconation of arylselenoethynes **1** and the configuration retention of both the starting alkenyl zirconium complexes and the alkenyl halides.

Vinylic selenides can couple with Grignard reagents in the presence of catalytic amount of nickel-phosphine complexes to afford the corresponding unsaturated hydrcarbons with loss of selenium-containing groups[14]. We reacted (E, E)-1-arylselenobutadienes **4** with Grignard reagents in the presence of $NiCl_2(PPh_3)_2$ and found that (E,E)-1,4-disubstituted-1,3-butadienes **5** were formed, which are shown in scheme 3. The investigation on the synthetic applications of (E,E)-1-arylselenobutadienes **4** is in progress.



**Scheme 2**

**Table 2** Synthesis of (E,E)-1,4-disubstituted-1,3-butadienes **5a** and **5b**

| Product | R | $Ar^1$ | m. p. (℃)[a,b] | Yield(%)[c,d] |
|---|---|---|---|---|
| **5a** | Ph | Ph | 147-148<br>(149-150) | 82 |
| **5b** | Ph | $4\text{-}MeC_6H_4$ | 154-155<br>(155-156) | 77 |

a. uncorrected; b. The melting points in parentheses shown below were cited from the literature[15]; c. isolated yield; d. $NiCl_2(PPh_3)_2$ (3% × 0.5mmol), (E,E)-1-arylselenobutadienes **4** (0.5mmol) and arylmagnesium bromides (2.0mmol) were stirred in THF at r.t. for 48h to afford (E,E)-1,4-disubstituted-1,3-butadienes **5**.

## EXPERIMENTAL

$^1H$ NMR spectra were recorded on a Bruker AC-P200(200M Hz) Spectrometer with $Me_4Si$ as the internal standard in $CDCl_3$. Mass spectra were obtained on a HP 5890 A mass spectrometer and IR spectra on a Shimadzu IR-435 instrument. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser. Solvent THF was distilled from sodium-benzophenone ketyl before use. $Cp_2Zr(H)Cl$ was prepared according to literature[13]. All reactions were carried out under nitrogen.

*General procedure for the synthesis of* **4a-d**:

To a dry 10ml flask charged with $Cp_2Zr(H)Cl$ (0.8mmol) was injected THF (3ml), followed by the addition of **1** (0.8mmol) at 0℃. The mixture was stirred at 0℃ for 40 min to yield a clear solution. It was then added alkenyl halide **3** (0.6mmol) and $Pd(PPh_3)_4$(0.6 × 5%mmol) and stirred at room temperature for 3 hrs. The resuting mixture was diluted with diethyl ether and after 5 min of additional stirring, the supernatant was filtered through a short plug of silica gel. After removal of solvent, the residue was purified by preparative TLC on silica gel (petroleum ether as eluent for **4a** and **4c**, diethyl ether/petroleum ether (1 : 20) for **4b** and **4d**.

*(E,E)-4-Phenyl-1-phenylseleno-1,3-butadiene* (**4a**):

m.p. 40-41℃; IR(KBr) υ($cm^{-1}$): 3040,1593,981,736,690,$^1H$ NMR δ(ppm): 724-735 (m,10H), 6.40-7.12(m,4H); MS m/z: 286($M^+$,21),128(100); Anal. Calcd. for $C_{16}H_{14}Se$: C,67.38; H,4.95. Found C,67.45; H,5.10.

*(E,E)-5-Methoxyl-1-phenylseleno-1,3-pentadiene* (**4b**):

IR(film) υ($cm^{-1}$): 3032,2904,1570,734,686; $^1H$ NMR δ(ppm): 7.25-7.51(m,5H), 6.24-6.73(m,3H), 5.64-5.71(m,1H), 3.94(d,2H), 3.31(s,3H); MS m/z: 254 ($M^+$,11), 97(100); Anal. Calcd. for $C_{12}H_{14}OSe$: C,56.94; H,5.57. Found C,56.83; H,5.72.

*(E,E)-4-Phenyl-1-(4-methylphenylseleno)-1,3-butadiene* (**4c**):
IR(film) υ(cm$^{-1}$): 3015, 1594, 970, 803, 687; $^1$H NMR δ(ppm): 7.06-7.49(m,9H), 6.45-6.86(m,4H), 2.39(s,3H); MS m/z: 300(M$^+$,26),128(100); Anal. Calcd. for $C_{17}H_{16}Se$: C,68.24; H,5.39. Found C,68.31; H,5.54.

*(E,E)-5-Methoxyl-1-(4-methylphenylseleno)-1,3-pentadiene* (**4d**):
IR(film) υ(cm$^{-1}$): 3012, 2908, 1600, 980, 804; $^1$H NMR δ(ppm): 7.12-7.45(q,4H), 6.20-6.71(m,3H), 5.63-5.71(m,1H), 3.95(d,2H), 3.35(s,3H), 2.27(s,3H); MS m/z: 268(M$^+$,20),97(100); Anal. Calcd. for $C_{13}H_{16}OSe$: C,58.44; H,6.04; Found C, 58.67; H,6.11.

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