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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(N) complexes 2, which are cross-coupled with alkenyl halides in the presence of Pd(PPh₃)₄ to afford (E,E)-1-arylselenobutadienes 4 in high yields. Copyright © 1996 Elsevier Science Ltd

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 amide¹, and are also valuable intermediates in the synthesis of more complex targets via Diels-Alder reaction².

In literature, we found the stereoselective synthesis of (E, E)-1-trimethylsilylbutadienes^{3,4}, (E,E)-1-phenylthiobutadienes⁵. However, there are few reports on the synthesis of (E,E)-1-arylselenobutadienes⁶.

Hydrozirconation⁷ can tolerate certain ether functionalities, such as OEt and OTHP group⁸, 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 (W) 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

Ar in 1	3		Product 4	Yield(%)*
	R	x		
Ph	Ph	Br	4a	82
Ph	Ph	Ι	4a	77
Ph	CH ₃ OCH ₂	Br	4b	86
$4-MeC_6H_4$	Ph	Br	4 c	80
$4-MeC_6H_4$	Ph	I	4 c	79
$4-MeC_6H_4$	CH ₃ OCH ₂	Br	4 d	88

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

a. isolated yield b. The configuration of double bonds were determined by ¹HNMR^{11,12}.

The alkenyl halides were prepared by hydrozirconation of 1-alkynes followed by trapping with electrophilic halogenation $(I_2 \text{ or } N\text{-bromosuccinimide})^{13}$.

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 groups¹⁴. We reacted (E, E)-1-arylselenobutadienes 4 with Grignard reagents in the presence of NiCl₂(PPh₃)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-1,5-butautilies 5a and 5b						
Product	R	Ar ¹	m.p.(°C) ^{a,b}	Yield (%) ^{c,d}		
5a	Ph	Ph	147-148 (149-150)	82		
5b	Ph	4-MeC ₆ H ₄	154-155 (155-156)	77		

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

a. uncorrected; b. The melting points in parentheses shown below were cited from the literature¹⁵; c. isolated yield; d. NiCl₂ (PPh₃)₂ ($3\% \times 0.5$ mmol), (E,E)-1-arylse-lenobutadienes 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 Me₄Si as the internal standard in CDCl₃. 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. Cp₂Zr(H)Cl was prepared according to literature¹³. 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°C. The mixture was stirred at 0°C for 40 min to yield a clear solution. It was then added alkenyl halide 3 (0.6mmol) and Pd(PPh_3)₄(0.6 $\times 5\%$ 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°C; IR(KBr) $v(cm^{-1})$; 3040,1593,981,736,690,¹H NMR $\delta(ppm)$; 724-735 (m,10H), 6.40-7.12(m,4H); MS m/z; 286(M⁺,21),128(100); Anal. Calcd. for C₁₆H₁₄Se: 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 C₁₂H₁₄OSe: 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) $v(cm^{-1})$: 3015, 1594, 970, 803, 687; ¹H NMR $\delta(ppm)$: 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; ¹H 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 C₁₃H₁₆OSe: C,58.44; H,6.04; Found C, 58.67; H,6.11.

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REFERENCES AND NOTES

- 1. Huang, Y.Z., Shi, L., Yang, J. and Zhang, J., Tetrahedron Lett., 1987, 28, 2159.
- 2. Arce, E., Carreno, M.C., Cid, M.B., Ruano, J.L.G., J. Org. Chem., 1994, 59, 3421.
- Fiandanese, V., Marchese, G., Mascolo, G., Naso, F. and Ronzini, L., Tetrahedron Lett., 1988, 29,3705.
- 4. Chan, T. H. and Li, J. S., J. Chem. Soc., Chem. Commun., 1982,696.
- 5. Naso, F., Pure Appl. Chem., 1988, 60, 79.
- 6. Comasseto, J. V. and Brandt, C. A., Synthesis, 1987, 146.
- (a) For a review containing pertinent references, see Schwartz, J., J. Organomet. Chem., Library, 1976, 1, 461; (b) Wailes, P. C., Weigold H. and Bell, A. P., J. Organomet. Chem., 1971, 27, 373.
- 8. Negishi, E. and Van Horn, D. E., J. Am. Chem. Soc., 1977,99, 3168.
- Negishi, E., Okukado, H., King, A.O., Van Horn, D.E., Spiegel, B.I., J. Am. Chem. Soc., 1978, 100, 2254.
- 10. Arylselenoethynes 1 were conveniently prepared by reacting diaryldiselenides with sodium acetylide in THF at 0°C in moderate yield.
- 11. Braga, A.L., Reckziegel, A. and silvera, C.C., Synth. Commun., 1994, 24, 1165.
- 12. Lee, C. W., Koh, Y. J. and Oh, D. Y., J. Chem. Soc., Perkin Trans. 1, 1994,717.
- 13. Schwartz, J. and Labinger, J.A., Angew. Chem. Int. Ed. Engl., 1976, 15, 333.
- 14. Okamura, H., Miura, M., Kosugi, K., and Takei, H., Tetrahedron Lett., 1980, 21, 87.
- The melting point of compound 5a was reported in the literature: Markl, G. and Merz, A., Synthesis, 1973, 295; the melting point of 5b was reported in the literature: Leznoff, C. C. and Hayward, R. J., Can. J. Chem., 1970, 48, 1842.

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