Palladium-Catalyzed Stereoselective Synthesis of (*E,E*)-1-Arylselenobutadienes

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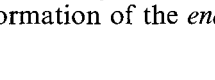
(*E*)-Vinylic zirconium(IV) complexes, readily obtainable via hydrozirconation of alk-1-ynes, react with (*E*)-1-halo-2-arylselenoethylenes in the presence of catalytic amounts of tetrakis(triphenylphosphane)palladium to produce (*E,E*)-1-arylselenobutadienes in high yields.

Stereodefined conjugated dienes represent a class of important intermediates and a variety of natural products of biological interest, such as Achillea amide[1] and Pellitorine.[2] The synthesis of dienes for use in the Diels–Alder reaction[3] is still an important challenge in synthetic organic chemistry.[4] One particularly attractive approach has been the incorporation of heteroatom substituents that can activate the diene,[5] thereby extending the range of workable dienophiles, and also provide a focal point for later synthetic elaboration.

To take advantage of the *endo* stereoselectivity, the *ortho*- and *para*-directing regioselectivity and the *cis* stereochemistry of the Diels–Alder cycloaddition,[6] it is implicit that the diene should be both stereochemically defined and configurationally stable under the reaction conditions. Thus, a 1,4-disubstituted acyclic diene of the type **1**, having the *E,E* stereochemistry and an *S-cis* planar conformation, is most able to overlap in the preferred *endo* transition state; other stereoisomers of **1**, such as the *E,Z*, the *Z,E*, and the *Z,Z* would encounter steric repulsion either in attaining the necessary *S-cis* conformation or in the formation of the *endo* transition state.



1

In the literature, we found the stereoselective synthesis of (*E,E*)-1-trimethylsilylbutadienes[7,8] and (*E,E*)-1-phenylthiobutadienes.[9] However, there are few reports on the synthesis of (*E,E*)-1-arylselenobutadienes.[10] There was a highly stereo- and regioselective procedure for the synthesis of conjugated dienes by a palladium-catalyzed reaction of alkenyl zirconium complexes with alkenyl halides.[11] We tried to employ the method to develop an efficient route to (*E,E*)-1-arylselenobutadienes **5**, and have indeed found that the selenium-containing conjugated diene synthesis shown in Scheme 1 can be successfully achieved with (*E*)-1-halo-2-arylselenoethylenes **4** in place of the corresponding alkenyl halides.

Table. Synthesis of Products **5a–d**

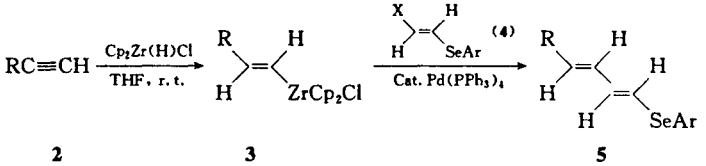
2	4	Product (5)	Yield (%)[a]
2a	**4a**	**5a**	71
2a	**4b**	**5b**	65
2a	**4c**	**5a**	82
2a	**4d**	**5b**	75
2b	**4a**	**5c**	73
2b	**4b**	**5d**	68
2b	**4c**	**5c**	78
2b	**4d**	**5d**	83

[a] Yield of isolated product

The yields of the (*E*)-alkenylzirconium derivatives obtained by reaction of $Cp_2Zr(H)Cl$ with alkynes in a 1 : 1 molar ratio have been typically in the range 75–90% by ^1H NMR.[12] Thus, it was necessary to use modest excesses of $Cp_2Zr(H)Cl$ and alkynes for the complete conversion of alkenyl halides into the desired cross-coupled products (see Table).

The starting materials, (*E*)-1-halo-2-arylselenoethylenes **4**, were prepared by hydrozirconation of arylselenoethynes, followed by trapping with iodine or *N*-bromosuccinimide (NBS), which is shown in Scheme 2.[13]

All products were fully characterized. The ^1H NMR of (*E*)-vinylic selenides give rise to a doublet at $\delta = 6-7$ with a coupling constant 14–16 Hz.[14] The *E,E* configuration of the products **5** is supported by $J_{H,H}$ of 14.6–15.7 Hz which could be measured.[15]

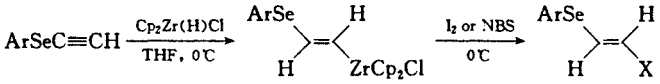


2 **3** **5**

2	a	b
R	Ph	CH_3OCH_2

4	a	b	c	d
X	Br	Br	I	I
Ar	Ph	4-MeC_6H_4	Ph	4-MeC_6H_4

Scheme 1



Ar = Ph, 4-MeC_6H_4; X = I, Br

Scheme 2

All reactions were carried out under N_2. THF was distilled from sodium benzophenone ketyl. Mps were uncorrected. ^{1}H NMR spectra were recorded on a AC-P 200 (200 MHz) spectrometer with TMS as internal standard in $CDCl_3$. IR spectra were taken on a Shimadzu IR-435 spectrometer. MS spectra were obtained on a HP 5890 A mass spectrometer and microanalyses were measured using a Yanaco MT-3CHN microelemental analyser.

Synthesis of 5a–d; General Procedure:

A mixture of $Cp_2Zr(H)Cl$ (0.8 mmol) and **2** (0.8 mmol) in THF (4 mL) was stirred at r.t. for 20 min. To the resulting solution was added **4** (0.6 mmol) and $Pd(PPh_3)_4$ (0.6 × 5% mmol) and this was stirred at r.t. for 3 h. It was then diluted with Et_2O and after 5 min of additional stirring, the supernatant liquid 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 (bp 30–60 °C) as eluent for **5a–b**, Et_2O/petroleum ether (1 : 20) for **5c–d**].

(E,E)-4-Phenyl-1-phenylselenobuta-1,3-diene **(5a)**: mp 40–41 °C.

IR (KBr): ν = 3041, 1591, 980, 734, 686 cm^{-1}.

^{1}H NMR: δ = 7.26–7.34 (m, 10H), 6.42–7.12 (m, 4H).

MS: m/z = 286.05 (M^+, 21.00), 128.20 (100.00).

Anal. Calcd. for $C_{16}H_{14}Se$: C, 67.38; H, 4.95. Found C, 67.05; H, 5.08.

(E,E)-4-Phenyl-1-(4-methylphenylseleno)buta-1,3-diene **(5b)**:

IR (film): ν = 3102, 1593, 982, 800, 687 cm^{-1}.

^{1}H NMR: δ = 7.05–7.49 (m, 9H), 6.42–7.85 (m, 4H); 2.39 (s, 3H).

MS: m/z = 300.05 (M^+, 25.93), 128.05 (100.00).

Anal. Calcd. for $C_{17}H_{16}Se$: C, 68.24; H, 5.39.

Found C, 68.53; H, 5.30.

(E,E)-5-Methoxy-1-phenylselenopenta-1,3-diene **(5c)**:

IR (film): ν = 3035, 2905, 1574, 993, 733, 686 cm^{-1}.

^{1}H NMR: δ = 7.29–7.50 (m, 5H), 6.25–6.74 (m, 3H); 5.64–5.72 (m, 1H), 3.95 (d, 2H), 3.30 (s, 3H).

MS: m/z = 254.00 (M^+, 11.33), 97.15 (100.00).

Anal. Calcd. for $C_{12}H_{14}OSe$: C, 56.94; H, 5.57. Found C, 56.82; H, 5.71.

(E,E)-5-Methoxy-1-(4-methylphenylseleno)penta-1,3-diene **(5d)**:

IR (film): ν = 3010, 2905, 1569, 978, 801 cm^{-1}.

^{1}H NMR: δ = 7.11–7.43 (q, 4H), 6.19–6.71 (m, 3H); 5.62–5.70 (m, 1H), 3.95 (d, 2H), 3.34 (s, 3H), 2.26 (s, 3H).

MS: m/z = 268.00 (M^+, 20.02), 97.05 (100.00).

Anal. Calcd. for $C_{13}H_{16}OSe$: C, 58.44; H, 6.04. Found C, 58.80; H, 6.38.

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