Chinese Journal of Chemistry, **2004**, *22*, 184—186

Article

Highly Stereoselective Synthesis of Phenylseleno- and *p*-Tolylsulfonyl Substituted 1,3-Dienes from Functionalized Allyl Alcohols

XIE, Mei-Hua[a,b](谢美华) HUANG, Xian*[,a,c](黄宪)

[a] *Department of Chemistry, Zhejiang University (Xixi Campus), Hangzhou, Zhejiang 310028, China*
[b] *Department of Chemistry, Anhui Normal University, Wuhu, Anhui 241000, China*
[c] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

Phenylseleno- and *p*-tolylsulfonyl substituted 1,3-dienes were conveniently prepared with high stereoselectivity by the elimination reaction of phenylseleno- and *p*-tolylsulfonyl substituted allyl alcohols in the presence of $BF_3 \cdot Et_2O$ in acetic anhydride. The products were characterized by ^1H NMR, MS, IR and elemental analysis. The single crystal structure of **2a** was determined by X-ray diffraction analysis.

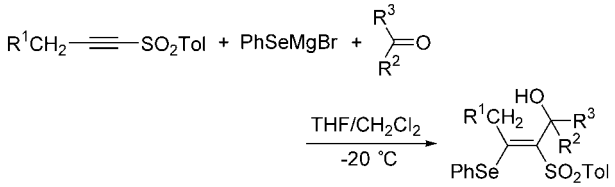
Keywords allyl alcohol, phenylseleno, *p*-tolylsulfonyl, 1,3-diene, stereoselectivity

Introduction

Heteroatom-substituted 1,3-dienes have been extensively studied because of their marked abilities to construct highly functionalized ring systems in cycloadditions.[1] For example, Danishefsky[2] developed 1-methoxy-3-trimethyl-siloxy-buta-1,3-diene which has led to many creative applications in complex organic synthesis. Padwa *et al.*[3] demonstrated that 1,3- and 2,3-bis(phenyl-sulfonyl)-1,3-butadienes are versatile building blocks in organic synthesis via reactions such as [4+2]-cycloadditions and 1,3-dipolar cycloadditions. In particular, dienes with two different heteroatoms, *e.g.* oxygen and sulfur,[4] or those with acylamino and sulfur[5] have received much attention because of their excellent reactivity and endo stereoselectivity. However, selenium-substituted 1,3-dienes with another heteroatom have been limited in study because they are difficult to prepare.[6]

Recently, we have reported a stereoselective synthesis of phenylseleno- and *p*-tolylsulfonyl substituted allyl alcohols from the Michael-Aldol tandem reaction of acetylenic sulfone, phenylselenomagnesium bromide and carbonyl compound (Scheme 1).[7] As an investigation on the application of the functionalized allyl alcohols in organic synthesis, we demonstrated that they are potential precursors of phenylseleno- and *p*-tolylsulfonyl substituted 1,3-dienes. We wish to report herein a simple and stereoselective synthesis of phenylseleno- and *p*-tolylsulfonyl substituted 1,3-dienes from allyl alcohols.

Scheme 1



Results and discussion

(*Z*)-3-Phenylseleno-2-(*p*-tolylsulfonyl)-1-(*p*-chlorophenyl)-2-octen-1-ol (**1a**) was chosen to optimize the reaction conditions. The reaction of **1a** with acetic anhydride in the presence of $BF_3 \cdot Et_2O$ (molar ratio=1∶1∶1) by using CH_2Cl_2 as solvent gave a complex stereoisomeric mixture of 3-phenylseleno-2-(*p*-tolylsulfonyl) substituted 1,3-dienes (determined from ^1H NMR spectra (400 MHz) of the crude reaction mixture). However, when $BF_3 \cdot Et_2O$ (0.5 mmol) was added to the solution of **1a** (0.5 mmol) in acetic anhydride (1 mL) at 0 ℃ and the resultant solution was stirred for 5 min, the product (1*E*,3*E*)-3-phenylseleno-2-(*p*-tolylsulfonyl)-1-(*p*-chlorophenyl)octa-1,3-diene (**2a**) was obtained in high yield with high stereoselectivity (isomeric purity≥95%) (Scheme 2). $BF_3 \cdot Et_2O$ and acetic anhydride are necessary to the elimination reaction. In case of the absence of $BF_3 \cdot Et_2O$ or acetic anhydride, no 1,3-diene was formed. Further studies showed that the reaction conditions are general for differently substituted allyl alcohols. The isomeric purities are higher than 90% (determined by ^1H NMR spectroscopy (400 MHz) of the crude reaction mixture). The results are summarized in Table 1.

* E-mail: huangx@mail.hz.zj.cn; Tel.: +86-571-88807077; Fax: +86-571-88807077
Received July 1, 2003; revised September 12, 2003; accepted October 21, 2003.
Project supported by the National Natural Science Foundation of China (No. 20272050).

Scheme 2

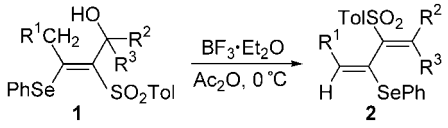


Table 1 Synthesis of phenylseleno- and *p*-tolylsulfonyl substituted 1,3-dienes

Entry	R^1	R^2	R^3	Time/min	Yield of **2**[a]/%
1	*n*-C_4H_9	H	*p*-ClC_6H_4	5	**2a** 96
2	*n*-C_4H_9	H	C_6H_5	5	**2b** 90
3	*n*-C_4H_9	H	*p*-$NO_2C_6H_4$	10	**2c** 94
4	*n*-C_4H_9	H	*p*-$CH_3OC_6H_4$	5	**2d** 90
5	*n*-C_4H_9	H	Styryl	5	**2e** 92
6	*n*-C_4H_9	CH_3	Styryl	5	**2f** 88
7	*n*-C_3H_7	H	*p*-ClC_6H_4	5	**2g** 94
8	*n*-C_3H_7	H	C_6H_5	5	**2h** 90

[a] Isolated yield of **2** based on **1**.

Table 1 shows that the elimination reaction of phenylseleno- and *p*-tolylsulfonyl substituted allyl alcohols processes smoothly to give phenylseleno- and *p*-tolylsulfonyl substituted 1,3-dienes in high yield with high stereoselectivity. Investigation of the crude reaction mixture by ^{1}H NMR spectroscopy (400 MHz) showed that the isomeric purities are higher than 90% (determined by the ^{1}H NMR spectra of the crude reaction mixture). R^2 can be proton (Entries 1—5, 7, 8) or alkyl (Entry 6); R^3 can be differently substituted aryl (Entries 1—4, 7, 8, Table 1) or styryl (Entries 5, 6, Table 1). When R^3 is styryl, conjugated triene **2e** or **2f** is obtained accordingly.

The 1*E*,3*E* configuration of product **2a** was verified by the NOESY spectrum. The NOESY spectra of **2a** show that there are the correlation between 1-H and the protons of *p*-tolylsulfonyl and the correlation between 4-H and protons of phenylseleno. The configuration was further confirmed by X-ray diffraction analysis (Figure 1). The bond length and bond angle is selectively listed in Table 2. The 3*E*,5*E* configuration of the conjugated trienes **2f** [(1*E*,3*E*,5*E*)-3-methyl-1-phenyl-4-(*p*-tolylsulfonyl)-5-phenylseleno-deca-1,3,5-triene] was also verified by the NOESY spectrum and the 1*E* configuration of **2f** was confirmed by the coupling constants of the vinylic protons (16.0 Hz). The configurations of the other products were deduced from those of **2a** and **2f**.

In conclusion, this paper describes a simple and straightforward method for preparing heteroatom (selenium and sulfur) substituted conjugated dienes in high yield with high stereoselectivity. The precursors can be obtained conveniently by the Michael-Aldol tandem reaction of acetylenic sulfone, phenylselenomagnesium bromide and carbonyl compound. The method has the advantages of simple procedures, mild reaction conditions, high yields and high stereoselectivity. The detailed mechanism and investigations into the synthetic applications of 1, 3-dienes **2** are now in progress.

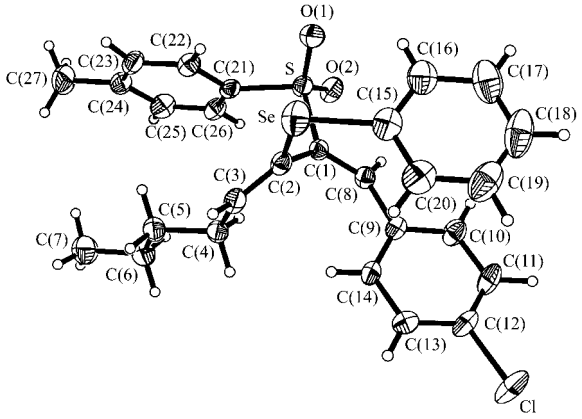


Figure 1 Molecular structure of compound **2a**.

Table 2 Selected bond lengths ($\times 10^{-1}$ nm) and bond angles (°) for **2a**

S—O(1)	1.4302(9)	C(21)-S-C(1)	106.73(10)
S—O(2)	1.4352(8)	C(15)-Se-C(2)	98.67(11)
S—C(21)	1.762(2)	C(8)-C(1)-C(2)	128.4(2)
S—C(1)	1.792(2)	C(8)-C(1)-S	114.99(19)
Se—C(15)	1.916(3)	C(2)-C(1)-S	116.47(16)
Se—C(2)	1.924(3)	C(3)-C(2)-C(1)	123.1(2)
C(1)—C(8)	1.332(3)	C(3)-C(2)-Se	118.9(2)
C(1)—C(2)	1.466(3)	C(1)-C(2)-Se	117.88(18)
C(2)—C(3)	1.329(4)	C(2)-C(3)-C(4)	126.2(3)
C(3)—C(4)	1.482(4)	C(2)-C(3)-H(1)	118.2(15)
C(3)—H(1)	0.976(7)	C(4)-C(3)-H(1)	115.0(15)
C(4)—C(5)	1.519(4)	C(3)-C(4)-C(5)	115.0(3)
C(5)—C(6)	1.498(5)	C(4)-C(5)-C(6)	113.0(3)
C(6)—C(7)	1.503(5)	C(5)-C(6)-C(7)	113.7(3)
C(8)—C(9)	1.470(3)	C(1)-C(8)-C(9)	129.8(2)
C(8)—H(11)	0.935(6)	C(16)-C(15)-C(20)	119.5(3)
		C(26)-C(21)-C(22)	120.2(2)

Experimental

Melting point was uncorrected. EIMS were determined with an HP5989B mass spectrometer. IR spectra were run on a Bruck vector 22 spectrometer. All ^{1}H NMR spectra were measured in $CDCl_3$ and recorded on a Brucker Avance-400 (400 MHz) spectrometer with TMS as the internal standard. X-ray crystallographic analysis was made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo Kα radiation (λ=0.071073 nm). The allyl alcohols were prepared by the reported method.[7]

General procedure for the synthesis of 2a—2h

$BF_3 \cdot Et_2O$ (0.5 mmol) was added to the solution of allyl alcohol **1** (0.5 mmol) in Ac_2O (1 mL) at 0 ℃. The reaction mixture was stirred for a given time and then poured into $CHCl_3$ (15 mL). The organic layer was washed with a saturated $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was removed *in vacuo*. The

residue was purified by preparative TLC on silica gel (hexane/ethyl acetate, 10 ∶ 1, *V* ∶ *V*) to afford the 1,3-diene **2**.

(1*E*,3*E*)-3-Phenylseleno-2-(*p*-tolylsulfonyl)-1-(*p*-chlorophenyl)octa-1,3-diene (2a) m.p. 89 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, J=8.2 Hz, 2H), 7.68 (s, 1H), 7.45—7.49 (m, 4H), 7.19—7.32 (m, 7H), 5.79 (t, J=7.3 Hz, 1H), 2.43 (s, 3H), 1.42—1.64 (m, 2H), 0.87—0.96 (m, 4H), 0.65 (t, J=7.0 Hz, 3H); IR (KBr) ν: 3030, 1595, 1348, 1149 cm^{-1}; MS *m*/*z* (%): 530 (M^+, ^{35}Cl, 2.86), 217 (M^+−PhSeH−SO_2Tol, ^{35}Cl, 100). Anal. calcd for $C_{27}H_{27}ClO_2SSe$: C 61.19, H 5.13; found C 61.35, H 5.38.

(1*E*,3*E*)-3-Phenylseleno-2-(*p*-tolylsulfonyl)-1-phenylocta-1,3-diene (2b) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, J=8.1 Hz, 2H), 7.76 (s, 1H), 7.51—7.57 (m, 4H), 6.95—7.31 (m, 8H), 5.76 (t, J=7.3 Hz, 1H), 2.39 (s, 3H), 1.46—1.57 (m, 2H), 0.78—0.93 (m, 4H), 0.62 (t, J=7.2 Hz, 3H); IR (film) ν: 3021, 1596, 1313, 1147, 757 cm^{-1}. MS *m*/*z* (%): 518 (M^+, ^{35}Cl, 3.10), 376 (M^+−PhSe, ^{35}Cl, 5.57), 205 (M^+−PhSeH−SO_2Tol, ^{37}Cl, 33.78,), 203 (M^+−PhSeH−SO_2Tol, ^{35}Cl, 100). Anal. calcd for $C_{27}H_{28}O_2SSe$: C 65.44, H 5.69; found C 65.58, H 5.75.

(1*E*,3*E*)-3-Phenylseleno-2-(*p*-nitrosulfonyl)-1-phenylocta-1,3-diene (2c) m.p. 120—122 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, J=8.4 Hz, 2H), 7.87 (d, J=8.0 Hz, 2H), 7.77 (s, 1H), 7.64—7.62 (m, 2H), 7.46—7.51 (m, 2H), 7.33—7.37 (m, 2H), 7.18—7.30 (m, 3H), 5.90 (t, J=7.2 Hz, 1H), 2.46 (s, 3H), 1.54—1.67 (m, 2H), 0.87—1.02 (m, 4H), 0.70 (t, J=7.2 Hz, 3H); IR (film) ν: 3022, 1596, 1346, 1148, 757 cm^{-1}; MS *m*/*z* (%): 541 (M^+, 2.6), 385 (M^+−SePh, 16.5), 228 (M^+−HSePh−SO_2Tol, 100). Anal. calcd for $C_{27}H_{27}NO_4SSe$: C 60.00, H 5.03, N 2.59; found C 59.82, H 5.08, N 2.62.

(1*E*,3*E*)-3-Phenylseleno-2-(*p*-tolylsulfonyl)-1-(*p*-methoxylphenyl)octa-1,3-diene (2d) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, J=8.0 Hz, 2H), 7.44—7.47 (m, 2H), 7.43 (s, 1H), 7.24—7.30 (m, 5H), 6.98—7.02 (m, 2H), 6.80—6.83 (m, 2H), 5.53 (t, J=6.8 Hz, 1H), 3.84 (s, 3H), 2.43 (s, 3H), 2.21—2.26 (m, 2H), 1.28—1.34 (m, 4H), 0.92 (t, J=7.0 Hz, 3H); IR (film) ν: 3060, 1602, 1301, 1257, 1146, 733 cm^{-1}; MS *m*/*z* (%): 526 (M^+, 2.0), 369 (M^+−SePh, 24.0), 213 (M^+−HSePh−SO_2Tol, 100). Anal. calcd for $C_{28}H_{30}O_3SSe$: C 63.99, H 5.75; found C 63.78, H 5.82.

(1*E*,3*E*,5*E*)-1-phenyl-4-(*p*-tolylsulfonyl)-5-phenylseleno-deca-1,3,5-triene (2e) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, J=8.0 Hz, 2H), 7.44—7.47 (m, 2H), 7.10—7.34 (m, 11H), 7.75 (d, J=15.2 Hz, 1H,), 6.48—6.55 (m, 1H), 5.68 (t, J=7.2 Hz, 1H), 2.44 (s, 3H), 2.35—2.39 (m, 2H), 1.29—1.37 (m, 4H), 0.94 (t, J=7.2 Hz, 3H). IR (film) ν: 3022, 1617, 1313, 1143, 757 cm^{-1}. MS *m*/*z* (%): 522 (M^+, 2.2), 365 (M^+−SePh, 14.1), 209 (M^+−HSePh−SO_2Tol, 100). Anal. calcd for $C_{29}H_{30}O_2SSe$: C 66.78, H 5.80; found C 66.65, H 5.86.

(1*E*,3*E*,5*E*)-3-methyl-1-phenyl-4-(*p*-tolylsulfonyl)-5-phenylseleno-deca-1,3,5-triene (2f) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J=8.0 Hz, 2H), 7.66 (d, J=8.8 Hz, 2H), 7.09—7.33 (m, 10H), 6.72 (d, J=16.0 Hz, 1H,), 6.59 (d, J=16.4 Hz, 1H), 5.80 (t, J=7.2 Hz, 1H), 2.31—2.61 (m, 5H), 2.22 (s, 3H), 1.36—1.40 (m, 4H), 0.93 (t, J=7.0 Hz, 3H); IR (film) ν: 3024, 1615, 1301, 1144, 734 cm^{-1}; MS *m*/*z* (%): 536 (M^+, 3.3), 379 (M^+−SePh, 19), 223 (M^+−HSePh−SO_2Tol, 100). Anal. calcd for $C_{30}H_{32}O_2SSe$: C 67.28, H 6.02; found C 67.40, H 6.11.

(1*E*,3*E*)-3-Phenylseleno-2-(*p*-tolylsulfonyl)-1-(*p*-chlorophenyl)hepta-1,3-diene (2g) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, J=8.0 Hz, 2H), 7.68 (s, 1H), 7.46—7.49 (m, 4H), 7.20—7.30 (m, 7H), 5.81 (t, J=7.3 Hz, 1H), 2.43 (s, 3H), 1.50—1.59 (m, 2H), 0.86—0.97 (m, 2H), 0.57 (t, J=7.3 Hz, 3H); IR (film) ν: 3024, 1629, 1314, 1147, 743 cm^{-1}; MS *m*/*z* (%): 518 (M^+, ^{37}Cl, 3.1), 516 (M^+, ^{35}Cl, 5.6), 361 (M^+−SePh, ^{37}Cl, 7.4), 359 (M^+−SePh, ^{35}Cl, 10.3), 205 (M^+−HSePh−SO_2Tol, ^{37}Cl, 33.8), 205 (M^+−HSePh−SO_2Tol, ^{35}Cl, 100). Anal. calcd for $C_{26}H_{25}ClO_2SSe$: C 60.53, H 4.88; found C 60.45, H 5.02.

(1*E*,3*E*)-3-Phenylseleno-2-(*p*-tolylsulfonyl)-1-phenylhepta-1,3-diene (2h) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, J=8.3 Hz, 2H), 7.76 (s, 1H), 7.51—7.57 (m, 4H), 7.19—7.34 (m, 8H), 5.77 (t, J=7.3 Hz, 1H), 2.41 (s, 3H), 1.46—1.59 (m, 2H), 0.86—0.95 (m, 2H), 0.54 (t, J=7.4 Hz, 3H); IR (film) ν: 3024, 1629, 1314, 1147, 755 cm^{-1}. MS *m*/*z* (%): 482 (M^+, 2.1), 325 (M^+−SePh, 22.5), 169 (M^+−HSePh−SO_2Tol, 100). Anal. calcd for $C_{26}H_{26}O_2SSe$: C 64.86, H 5.44; found C 64.72, H 5.51.

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(E0307016 PAN, B. F.)