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Highly Stereoselective Three-Component Reactions of Phenylselenomagnesium Bromide, Acetylenic Sulfones, and Saturated Aldehydes/Ketones or α,β-Unsaturated Enals or Enones

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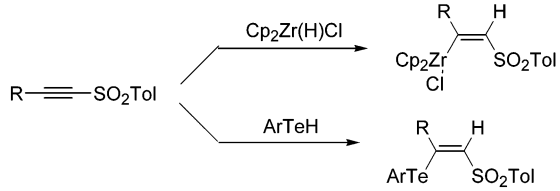
β-Phenylseleno-α-tolylsulfonyl-substituted alkenes were synthesized via the three-component conjugate−nucleophilic addition of acetylenic sulfones, phenylselenomagnesium bromide, and carbonyl compounds, such as aldehydes, aliphatic ketones, or α,β-unsaturated enals or enones. The reaction is highly regio- and stereoselective with moderate to good yields. Functionalized allylic alcohols were obtained in the case of aldehydes and aliphatic ketones. In the case of α,β-unsaturated enones, functionalized allylic alcohols or functionalized γ,δ-unsaturated ketones were obtained, depending on the structures of the ketones.

Introduction

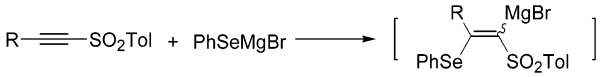
Stereodefined vinyl sulfones are important synthetic intermediates due to the presence of the carbon−carbon double bonds and the carbon−sulfur bonds.[1] We have shown that the hydrozirconation and hydrotelluration of 1-alkynyl sulfones afforded stereodefined 1-alkenyl sulfones (Scheme 1).[2,3]

Organomagnesium reagents[4] and organic selenides[5] are important reagents in organic chemistry and have been extensively studied. However, there are only limited reports on the reaction of magnesium selenolate.[6] Back and co-workers have reported that β-(phenylseleno)vinyl sulfones can be synthesized from the selenosulfonation of alkynes or the addition of organocopper reagents to 1-phenylseleno-2-(*p*-tolylsulfonyl)ethyne.[7] On the basis of our results (Scheme 1), we are interested in the selenomagnesiation of 1-alkynyl sulfones leading to 1-alkenyl sulfones with an extra Se-containing functional group and a C−Mg bond, providing that the issues of regio- and stereoselectivity can be addressed (Scheme 2).

SCHEME 1



SCHEME 2



In a preliminary communication, we have observed that the three-component reaction of acetylenic sulfones, phenylselenomagnesium bromide, and aldehydes afforded β-(phenylseleno)vinyl sulfones with high stereoselectivity.[8] In this paper, we wish to report the three-component reaction of phenylselenomagnesium bromide, acetylenic sulfones, and saturated aldehydes/ketones or α,β-unsaturated enals or enones in detail.

Results and Discussion

Two-Component Reaction of Phenylselenomagnesium Bromide and 1-Phenyl-2-(*p*-tolylsulfonyl)ethyne. We first investigated the conjugate addition of phenylselenomagnesium bromide to 1-phenyl-2-(*p*-tolylsulfonyl)ethyne. At −20 °C, when 1-phenyl-2-(*p*-tolylsulfonyl)ethyne (**1a**) was added to the THF solution of phenylselenomagnesium bromide (**2**) and stirred for 5

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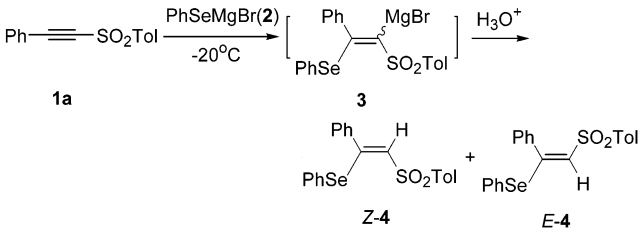
TABLE 1. Reaction of Phenylselenomagnesium Bromide with 1-Phenyl-2-(*p*-tolylsulfonyl)ethyne[a]



entry	solvent	time (min)	yield (%)[b]	ratio of Z/E[b]
1	THF	5	70	2/1
2	THF/CH_2Cl_2	5	76	3/1
3	THF/CH_2Cl_2	10	72	2.2/1
4	THF/CH_2Cl_2	20	70	1.5/1
5	THF/CH_2Cl_2	30	70	1.3/1
6	THF/CH_2Cl_2	40	68	1.1/1

[a] The reaction was carried out at −20 °C using **1a** (0.5 mmol) and **2** (0.6 mmol). [b] Determined by 400 MHz ^{1}H NMR analysis of the crude reaction mixture.

min followed by protonolysis, the expected product, 1-phenyl-1-phenylseleno-2-(*p*-tolylsulfonyl)ethene **4**, was obtained in 70% yield with a ratio of *Z*/*E* = 2/1 (entry 1, Table 1). When the reaction was carried out in THF/CH_2Cl_2 (v/v = 1/4), the stereoselectivity was better (the ratio of *Z*/*E* = 3/1) (entry 2, Table 1). The ratio of *Z*/*E* decreased with prolonged reaction time (entries 3−6, Table 1).

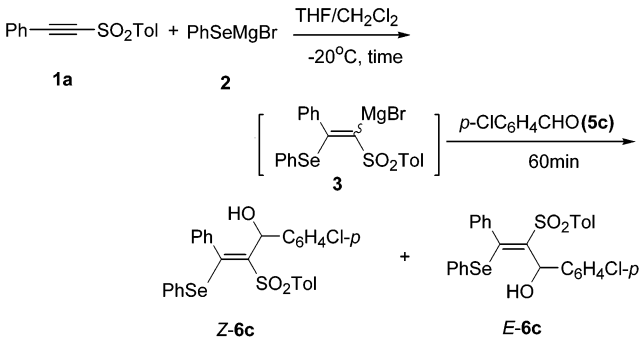
Z-**4** was a known compound; however, the ^{1}H NMR data observed here are quite different from what was published in the literature.[7a] Thus, the structure of *Z*-**4** was further established unambiguously by an X-ray diffraction study.[9] The structure of *E*-**4** was characterized by ^{1}H NMR spectral data, which is identical to what was published in the literature.[7b]

Stereoselective Three-Component Reaction of Phenylselenomagnesium Bromide, Acetylenic Sulfones, and Aldehydes. When *p*-chlorobenzaldehyde (**5c**) was added to the solution of 1-phenyl-2-(*p*-tolylsulfonyl)-ethyne (**1a**) and magnesium selenolate (**2**) at −20 °C in THF/CH_2Cl_2 (which had been stirred for 10 min) and stirred for 60 min, the adduct 3-phenyl-3-phenylseleno-2-(*p*-tolylsulfonyl)-1-(*p*-chlorophenyl)-2-propen-1-ol (**6c**) was formed in 75% yield with a *Z*/*E* ratio of 2.7/1 (entry 1, Table 2). With prolonged reaction time for mixing **1a** and the magnesium selenolate **2**, the ratio of *Z*/*E* dropped (entries 2−4, Table 2).

When *p*-chlorobenzaldehyde (**5c**) was added directly to the solution of phenylselenomagnesium bromide in THF/CH_2Cl_2 at −20 °C with stirring for 3 h, the corresponding 1,2-addition product **7** was not detected in the ^{1}H NMR spectrum of the crude reaction mixture. *p*-Chlorobenzaldehyde (**5c**) was recovered in 82% yield and diphenyl diselenide was obtained in 95% yield (Scheme 3). The results show that phenylselenomagnesium bromide (**2**) can react with 1-phenyl-2-(*p*-tolylsulfonyl)ethyne (**1a**) preferably to form the vinylmagnesium intermediate in

(9) Crystal data for *Z*-**4**: $C_{21}H_{18}O_2SSe$, MW = 413.37, monoclinic, space group $P2_1/n$, a = 12.574(4) Å, b = 12.087(3) Å, c = 13.132(5) Å; α = 90°, β = 107.973(4)°, γ = 90°. V = 1898.5(9) Å^3, T = 293 K, Z = 4, D_c = 1.446 g cm^{-1}, μ = 2.098 mm^{-1}, λ = 0.71073 Å; F(000) 840, 3351 independent reflections (R_{int} = 0.0380), 7684 reflections collected; refinement method, full-matrix least-squares on F^2; goodness-of-fit on F^2 =1.012; final R indices [$I > 2\sigma(I)$] R_1 = 0.0484, wR_2 = 0.1085.

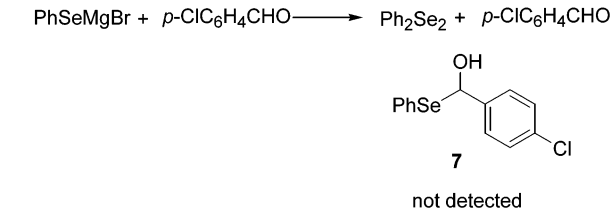
TABLE 2. Conjugate Addition of 1-Phenyl-2-(*p*-Tolylsulfonyl)ethyne, Phenylselenomagnesium Bromide and *p*-Chlorobenzaldehyde[a]



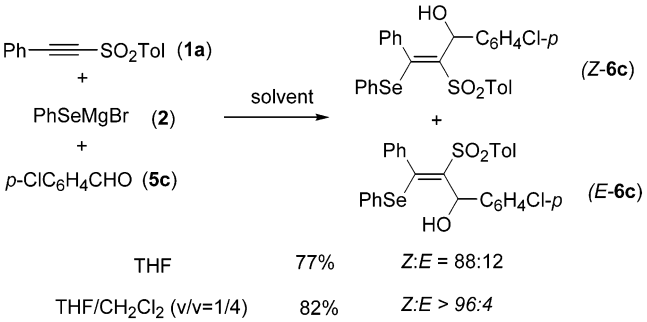
entry	time (min)	yield of **6c** (%)[b]	ratio of *Z*/*E*[b]
1	10	75	2.7/1
2	20	70	1.5/1
3	30	65	1.4/1
4	50	65	1/1

[a] The reaction was carried out at −20 °C using **1a** (0.5 mmol), **2** (0.6 mmol) and **5c** (0.5 mmol). [b] Determined by 400 MHz ^{1}H NMR spectra.

SCHEME 3



SCHEME 4

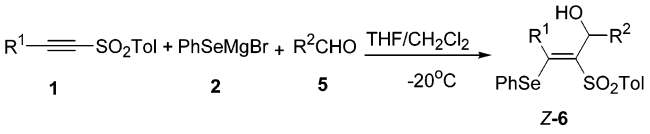


the one-pot reaction of **1a**, **2**, and **5c.** So it is possible for **5c** to capture the vinylmagnesium intermediate **3** immediately in hope of improving the stereoselectivity.

In fact, it is interesting to note that 3-phenyl-3-phenylseleno-2-(*p*-tolylsulfonyl)-1-(*p*-chlorophenyl)-2-propen-1-ol (**6c**) was afforded in 77% yield with a *Z*/*E* ratio of 88/12 when 1-phenyl-2-(*p*-tolylsulfonyl)ethyne (**1a**) and *p*-chlorobenzaldehyde (**5c**) were added simultaneously to the solution of phenylselenomagnesium bromide (**2**) in THF. Furthermore, with the addition of CH_2Cl_2 as the cosolvent, the reaction at −20 °C afforded **6c** in 82% yield with a *Z*/*E* ratio as high as >96/4 (Scheme 4), indicating a dramatic solvent effect.

Further studies showed that the reaction is general for differently substituted acetylenic sulfones and aldehydes: R^1 can be an alkyl (entries 2, 4, 5, 7, 8, 10, 11,

TABLE 3. Three-Component Reaction of Acetylenic Sulfones with Phenylselenomagnesium Bromide and Aldehydes[a]



1 2 5 *Z*-6

entry	R^1	R^2	time (min)	yield of *Z*-**6** (%) (*Z*/*E*)[b]
1	Ph	*p*-$NO_2C_6H_4$	50	80 (**6a**, >96/4)
2	*n*-C_5H_{11}	*p*-$NO_2C_6H_4$	50	78 (**6b**, >96/4)
3	Ph	*p*-ClC_6H_4	50	82 (**6c**, >96/4)
4	*n*-C_4H_9	*p*-ClC_6H_4	70	82 (**6d**, >99/1)
5	*n*-C_5H_{11}	*p*-ClC_6H_4	60	83 (**6e**, >98/2)
6	Ph	Ph	50	76 (**6f**, >98/2)
7	*n*-C_4H_9	Ph	60	82 (**6g**, >98/2)
8	*n*-C_5H_{11}	Ph	60	88 (**6h**, >98/2)
9	Ph	*p*-$CH_3OC_6H_4$	55	84 (**6i**, >98/2)
10	*n*-C_4H_9	*p*-$Me_2NC_6H_4$	50	76 (**6j**, >99/1)
11	*n*-C_5H_{11}	*p*-$CH_3OC_6H_4$	70	73 (**6k**, >99/1)
12	Ph	2-furyl	80	89 (**6l**, >97/3)
13	*n*-C_4H_9	2-furyl	80	85 (**6m**, >99/1)
14	*n*-C_5H_{11}	2-furyl	80	89 (**6n,** >96/4)
15	Ph	*n*-C_4H_9	75	85 (**6o**, >97/3)
16	*n*-C_5H_{11}	*n*-C_4H_9	70	76 (**6p**, >97/3)
17	*n*-C_4H_9	styryl	90	74 (**6q,** >97/3)
18	*n*-C_5H_{11}	styryl	90	88 (**6r**, >96/4)
19	Ph	vinyl	70	60 (**6s**, >96/4)
20	Ph	propenyl	70	75 (**6t**, >96/4)

[a] The reaction was carried out at −20 °C by adding **1** (0.5 mmol), **2** (0.6 mmol), and **5** (0.5 mmol) simultaneously in THF/CH_2Cl_2 (v/v =1/4). [b] Isolated yield of purified *Z*-**6** based on **1**. The ratio of *Z*/*E* was determined by 400 MHz ^{1}H NMR spectra of the unpurified reaction mixture.

13, 14, and 16−18, Table 3) or phenyl group (entries 1, 3, 6, 9, 12, 15, 19, and 20, Table 3); R^2 can be aryl (entries 1−11, Table 3), heteroaryl (entries 12−14, Table 3), and alkyl groups (entries 15 and 16, Table 3). Furthermore, it was interesting to note that even with 2-enals, the reaction occurred highly chemoselectively in a 1,2-addition manner (entries 17−20, Table 3).

The structures of these compounds were affirmatively characterized via ^{1}H NMR spectra and the NOESY experiment of *Z*-**6e** and the X-ray diffraction analysis of *Z*-**6f**.[10]

Stereoselective Three-Component Reaction of Acetylenic Sulfones, Phenylselenomagnesium Bromide, and Ketones. When 1-phenyl-2-(*p*-tolylsulfonyl)-ethyne (**1a**) and 2-pentanone (**8a**) were added simultaneously to the solution of phenylselenomagnesium bromide in THF/CH_2Cl_2, the 1,2-addition product (*Z*)-3-methyl-2-(*p*-tolylsulfonyl)-1-phenyl-1-phenylseleno-1-hexen-3-ol (*Z*-**9a**) was obtained in 70% yield with a high stereoselectivity (*Z*/*E* > 95/5). The reaction can be extended to other aliphatic ketones, such as 2-butanone and cyclohexanone. With alkyl-substituted acetylenic sulfone, similar results were observed. The results are summarized in Table 4. However, when aliphatic ketones were replaced by acetophenone, the expected three-component reaction did not occur and compound 1-phenyl-1-phenylseleno-2-(*p*-tolylsulfonyl)ethene (**4**) was formed surprisingly in 75% yield as the single *Z* isomer together with 3-hydroxy-1,3-diphenyl-1-butanone. 3-Hydroxy-1,3-diphenyl-1-butanone was formed by the self-condensation of acetophenone due to the steric hindrance of the phenyl group (see also the results in Table 6). Acetophenone was acting as an in situ proton source to generate *Z*-1-phenyl-1-phenylseleno-2-(*p*-tolylsulfonyl)ethene (*Z*-**4**) and the magnesium enolate intermediate **10**, which further reacted with acetophenone, leading to 3-hydroxy-1,3-diphenyl-1-butanone (Scheme 5).

The corresponding reaction with α,β-unsaturated ketone depends on the steric effect around the carbonyl group. The reaction of α,β-unsaturated aliphatic enones gave 1,2-adducts—substituted allyl alcohols *Z*-**12**—stereoselectively,[11] while the reaction of α,β-unsaturated aromatic enones gave 1,4-adducts—substituted γ,δ-unsaturated ketones *Z*-**14**—stereoselectively[12] (determined from the ^{1}H NMR spectra of the crude reaction mixture). The results are summarized in Tables 5 and 6, respectively. Compared with aldehydes, the reactions of ketones were slower to afford adducts in lower yields. In these cases, small amounts of 1-phenyl-1-phenylseleno-2-(*p*-tolylsulfonyl)ethene (**4**) (8−12%) and the unreacted ketones (5−10%) were detected.

Conclusion

In conclusion, we have demonstrated that the three-component reaction of phenylselenomagnesium bromide, acetylenic sulfones, and carbonyl compounds afforded polysubstituted alkenes in high stereoselectivity. Further studies on the application of the reaction are now in progress in our laboratory.

Experimental Section

General Techniques. All the solid products were recrystallized from ethyl acetate and hexanes, and the melting points are uncorrected. All reactions were carried out under a nitrogen atmosphere. THF was distilled from sodium/benzophenone. CH_2Cl_2 was distilled from calcium hydride; ^{1}H NMR spectra were measured at 400 MHz and all ^{13}C NMR spectra were measured at 100 or 125 MHz in $CDCl_3$ with TMS as the internal standard. Acetylenic sulfones[13] and α,β-unsaturated ketones[14] were prepared by literature methods.

The Two-Component Reaction of Phenylselenomagnesium Bromide with Acetylenic Sulfones. Preparation of 4. To a colorless solution of phenylselenomagnesium bromide (0.6 mmol) in THF/CH_2Cl_2 (v/v = 1:4, 5 mL) was added acetylenic sulfone (0.5 mmol) at −20 °C with stirring. The reaction mixture was stirred at −20 °C for a given time. Then the reaction was quenched with saturated NH_4Cl and extracted with CH_2Cl_2. The organic phase was washed with saturated brine and dried over $MgSO_4$. After filtration and

(10) Crystal data for *Z*-**6f**: $C_{28}H_{24}O_3SSe$, MW = 519.49, monoclinic, space group $P2_1/n$, a = 7.0710(4) Å, b = 14.6604(9) Å, c = 24.3432(5) Å; α = 90°, β = 94.7550(10)°, γ = 90°. V = 2514.8(3) Å^3, T = 293 K, Z = 4, D_c = 1.372 g cm^{-1}, μ = 1.603 mm^{-1}, λ = 0.71073 Å; F (000) 1064, 4688 independent reflections (R_{int} = 0.0754), 13 113 reflections collected; refinement method, full-matrix least-squares on F^2; goodness-of-fit on F^2 = 0.657; final R indices [$I > 2\sigma(I)$] R_1 = 0.0371, wR_2 = 0.0499.

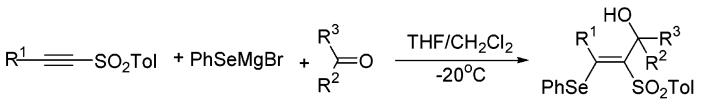
(11) For the synthesis of substituted allyl alcohols, see: Havránek, M.; Dvořák, D. *J. Org. Chem.* **2002**, *67*, 2125 and references therein.

(12) (a) For the Michael addition of 1-alkenylmetallic reagents with α,β-unsaturated ketones, see: Satoh, Y.; Serizawa, H.; Hara, S.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 5225 and references therein. (b) For metal-catalyzed Claisen rearrangement of allylic ether, see: Higashino, T.; Saleaguchi, S.; Ishii, Y. *Org. Lett.* **2000**, *2*, 4193; Renter, J. M.; Salomon, R. G. *J. Org. Chem.* **1977**, *42*, 3360.

(13) Truce, W. E.; Wolf, G. C. *J. Org. Chem.* **1971**, *36*, 1727.

(14) (a) Gilman, H. *Organic Synthesis*, 2nd ed.; Queen's College: Flushing, NY, 1956; Collect Vol. I, p 77. (b) Mariella, R. P.; Raube, R. R. *J. Am. Chem. Soc.* **1952**, *74*, 521. (c) Brown, C. D., Chong J. M.; Shen, L. X. *Tetrahedron* **1999**, *55*, 14233.

TABLE 4. Three-Component Reaction of Acetylenic Sulfones with Phenylselenomagnesium Bromide and Aliphatic Ketones[a]

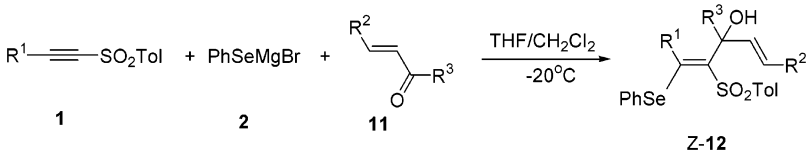


1 2 8 Z-9

entry	R^1	R^2	R^3	time (h)	yield of *Z*-**9** (%) (*Z*/*E*) [b]
1	Ph	CH_3	*n*-C_3H_7	3	70 (*Z*-**9a**, 95/5)
2	*n*-C_5H_{11}	CH_3	*n*-C_3H_7	3	79 (*Z*-**9b,** 96/4)
3	Ph	$-(CH_2)_5-$		3.5	65 (*Z*-**9c,** 96/4)
4	*n*-C_5H_{11}	$-(CH_2)_5-$		3.5	81 (*Z*-**9d,** 95/5)
5	Ph	CH_3	CH_3CH_2	3	69 (*Z*-**9e,** 95/5)

[a] The reaction was carried out at −20 °C by adding 1 (0.5 mmol), **2** (0.6 mmol), and **8** (0.5 mmol) simultaneously in THF/CH_2Cl_2 (v/v =1/4). [b] Isolated yield of purified *Z*-**9** based on **1**. The ratio of *Z*/*E* was determined by 400 MHz ^{1}H NMR spectra of the unpurified reaction mixture.

TABLE 5. Reaction of Acetylenic Sulfones with Phenylselenomagnesium Bromide and α,β-Unsaturated Aliphatic Ketones[a]



1 2 11 Z-12

entry	R^1	R^2	R^3	time (h)	yield of *Z*-**12** (%) (*Z*/*E*) [b]
1	Ph	*p*-$NO_2C_6H_4$-	CH_3	5	59 (*Z*-**12a**, 96/4)
2	Ph	Ph	CH_3	3	59 (*Z*-**12b,** 97/3**)**
3	*n*-C_5H_{11}	Ph	CH_3	3	59 (*Z*-**12c**, 95/5)
4	Ph	Ph	*n*-C_3H_7	3	56 (*Z*-**12d**, 96/4)
5	Ph	$-(CH_2)_3-$		2.5	73 (*Z*-**12e**, 98/2)
6	*n*-C_5H_{11}	$-(CH_2)_3-$		3	65 (*Z*-**12f**, 98/2)

[a] A mixture of 1 (0.5 mmol), **2** (0.6 mmol), and **11** (0.5 mmol) in 5 mL of THF/CH_2Cl_2 (1/4 v/v) was stirred at −20 °C. [b] Isolated yield of purified *Z*-**12** based on **1**. The ratio of *Z*/*E* was determined by 400 MHz ^{1}H NMR spectra of the unpurified reaction mixture.

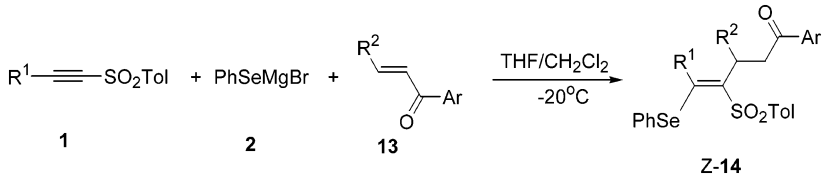
removal of the solvent in vacuo, the crude product was purified with flash chromatography (silica/hexanes−ethyl acetate 10:1 v/v) and the desired adduct 1-phenyl-1-phenylseleno-2-(*p*-tolylsulfonyl)ethene **(4)** was obtained.

(*Z*)-1-Phenyl-1-phenylseleno-2-(*p*-tolylsulfonyl)-ethene (*Z*-4): mp 132−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.12−7.03 (m, 8H), 6.97 (t, J = 7.5 Hz, 2H), 6.76 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 143.9, 137.9, 137.3, 135.3, 129.2, 128.3, 128.1, 128.0, 127.64, 127.6, 127.2, 127.1, 21.1; IR (KBr) 1595, 1320, 1142 cm^{-1}; MS (EI) *m*/*z* (%) 414 (24.7, M^+), 257 (15.1, M^+ − PhSe), 102 (13.6, M^+ − PhSe − SO_2Tol), 91 (100, $C_6H_5CH_2^+$). Anal. Calcd for $C_{21}H_{18}O_2SSe$: C, 61.02; H, 4.39. Found: C, 61.02; H, 4.37.

(*E*)-1-Phenyl-1-phenylseleno-2-(*p*-tolylsulfonyl)-ethene (*E*-4): mp 149 °C (lit.[2b] mp 152 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.2 Hz, 2H), 7.44−7.38 (m, 3H), 7.32−7.24 (m, 5H), 7.19 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.16 (s, 1H), 2.36 (s, 3H); IR (KBr) 1594, 1321, 1142 cm^{-1}; MS (EI) *m*/*z* (%) 414 (23.4, M^+), 257 (18.6, M^+ − PhSe), 102(8.6, M^+ − PhSe − SO_2Tol,), 91 (100, $C_6H_5CH_2^+$).

The Tandem Reaction of Phenylselenomagnesium Bromide with Acetylenic Sulfones and Aldehydes. Preparation of 6. General Procedure. To a colorless solution of phenylselenomagnesium bromide (0.6 mmol) in THF/CH_2Cl_2 (v/v = 1:4, 5 mL), prepared in situ from phenylmagnesium bromide and powder selenium, were added acetylenic sulfone (0.5 mmol) and aldehyde (0.5 mmol) at −20 °C with stirring.

TABLE 6. Reaction of Acetylenic Sulfones with Phenylselenomagnesium Bromide and α,β-Unsaturated Aromatic Ketones[a]

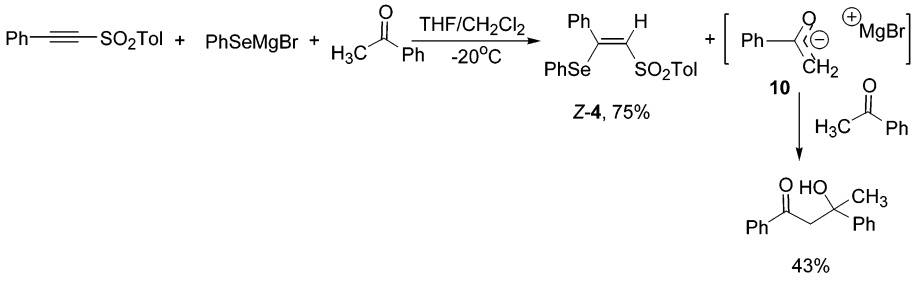


1 2 13 Z-14

entry	R^1	R^2	Ar	time (h)	yield of *Z*-**14** (%) (*Z*/*E*)[b]
1	Ph	Ph	Ph	4.5	63 (*Z*-**14a**, >95/5)
2	Ph	Ph	*p*-$CH_3OC_6H_4$	4	69 (*Z*-**14b**, >96/4)
3	Ph	*p*-$CH_3OC_6H_4$	Ph	4	68 (*Z*-**14c**, >95/5)
4	Ph	*p*-ClC_6H_4	*p*-$CH_3C_6H_4$	3.5	57 (*Z*-**14d**, >96/4)
5	Ph	CH_3	Ph	3	55 (*Z*-**14e**, >96/4)
6	*n*-C_5H_{11}	Ph	*p*-$CH_3OC_6H_4$	3.5	70 (*Z*-**14f**, 96/4)
7	*n*-C_5H_{11}	Ph	Ph	3.5	57 (*Z*-**14g**, >95/5)

[a] Mixture of **1** (0.5 mmol), **2** (0.6 mmol), and **13** (0.5 mmol) in 5 mL of THF/CH_2Cl_2 (1/4 v/v) was stirred at −20 °C. [b] Isolated yield of purified *Z*-**14** based on **1**. The ratio of *Z*/*E* was determined by 400 MHz ^{1}H NMR spectra of the unpurified reaction mixture.

SCHEME 5



The reaction mixture turned to a pale yellow solution, which was maintained stirring at −20 °C for 50−90 min. After the reaction was complete (monitored by TLC), the reaction was quenched with saturated NH_4Cl and extracted with CH_2Cl_2. The organic phase was washed with saturated brine and dried over $MgSO_4$. After filtration and removal of the solvent in vacuo, the crude product was purified with flash chromatography (silica/hexanes−ethyl acetate 8:1 v/ v) and the desired tandem adduct **6** was obtained. (*Z*)-3-Phenyl-3-phenylseleno-2-(*p*-tolylsulfonyl)-1-(*p*-nitrophenyl)-2-propen-1-ol (*Z*-**6a**): mp 180−181°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.12−7.08 (m, 1H), 7.02−6.93 (m, 8H), 6.82 (s, 1H), 5.56 (d, J = 11.0 Hz, 1H), 4.32 (d, J = 11.1 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 148.4, 146.9, 144.9, 138.0, 137.0, 136.8, 136.2, 129.3, 128.8, 128.5, 128.2, 127.8, 127.7, 126.5, 123.1, 73.1, 21.6; IR (KBr) 3478, 1517, 1343, 1260, 1134 cm^{-1}; MS (EI) *m*/*z* (%) 408 (24.0, M^+ − PhSe), 252 (59.2, M^+ − PhSeH − SO_2Tol), 91 (100, $C_6H_5CH_2^+$). Anal. Calcd for $C_{28}H_{23}NO_5SSe$: C, 59.58; H, 4.11; N, 2.48. Found: C, 59.40; H, 4.25; N, 2.52.

The Three-Component Reaction of Phenylselenomagnesium Bromide with Acetylenic Sulfones and Ketones. Preparation of 9, 12, or 14. General Procedure. To a colorless solution of phenylselenomagnesium bromide (0.6 mmol) in THF/CH_2Cl_2 (v/v = 1:4, 5 mL) were added acetylenic sulfone (0.5 mmol) and ketone (0.5 mmol) at −20 °C with stirring. The reaction mixture turned to a pale yellow solution, which was maintained stirring at −20 °C for 2.5−5 h. After usual workup, the desired tandem adduct **9**, **12**, or **14** was obtained.

(*Z*)-3-Methyl-2-(*p*-tolylsulfonyl)-1-phenyl-1-phenylseleno-1-hexen-3-ol (*Z*-9a): mp 121−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 6.93−6.81 (m, 7H), 6.75 (s, 1H), 6.64 (d, J = 6.34 Hz, 1H), 4.48 (br, 1H), 2.48 (s, 3H), 1.47−1.42 (m, 2H), 1.26−1.18 (m, 2H), 1.12 (s, 3H), 0.72 (t, J = 7.26 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 143.8, 142.1, 139.4, 137.6, 137.5, 129.6, 129.1, 128.5, 128.4, 128.1, 127.7, 127.6, 127.3, 127.0, 126.7, 78.4, 45.1, 30.8, 21.7, 17.0, 13.9; IR (KBr) 3549, 1276, 1139 cm^{-1}; MS (EI) *m*/*z* (%) 343 (14.1, M^+ − PhSe,), 187 (13.9, M^+ − PhSeH − SO_2Tol), 91 (100, $PhCH_2^+$). Anal. Calcd for $C_{26}H_{28}O_3SSe$: C, 62.52; H, 5.65. Found: C, 62.39; H, 5.92.

(*Z*)-3-(*p*-Nitrostyryl)-2-(*p*-tolylsulfonyl)-1-phenyl-1-phenylseleno-1-buten-3-ol (*Z*-12a): mp 136−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.3 Hz, 2H), 8.04 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 7.03−6.99 (m, 2H), 6.86−6.82 (m, 3H), 6.75−6.69 (m, 3H), 6.58 (t, J = 7.5 Hz, 1H), 6.45 (d, J = 8.5 Hz, 1H), 6.33 (d, J = 16.0 Hz, 1H), 5.96 (d, J = 16.0 Hz, 1H), 5.12 (s, 1H), 2.51 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 146.2, 143.7, 142.6, 141.1, 139.2, 138.4, 137.0, 136.6, 128.7, 128.4, 128.3, 128.1, 127.7, 127.4, 127.3, 127.2, 126.8, 126.5, 126.4, 124.5, 123.0, 76.3, 30.1, 21.2; IR (KBr) 3460, 1516, 1341, 1281, 1134 cm^{-1}; MS (EI) *m*/*z* (%) 448 (3.12, M^+ − PhSe), 292 (20.33, M^+ − PhSeH − SO_2Tol), 91 (100, $PhCH_2^+$). Anal. Calcd for $C_{31}H_{27}NO_5SSe$: C, 61.59; H, 4.50; N, 2.31. Found: C, 61.32; H, 4.81; N, 2.42.

(*Z*)-1,3,5-Triphenyl-4-(*p*-tolylsulfonyl)-5-phenylseleno-4-penten-1-one (*Z*-14a): mp 150−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.59−7.53 (m, 3H), 7.43−7.39 (m, 2H), 7.11−7.0 (m, 8H), 6.94−6.90 (m, 7H), 6.75−6.67 (br, 2H), 4.84 (dd, J = 9.7 Hz, 3.9 Hz, 1H), 4.37−4.30 (m, 1H), 3.40 (dd, J = 18.1 Hz, 3.9 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 154.5, 143.9, 139.7, 139.1, 138.6, 137.5, 137.4, 136.6, 133.0, 129.1, 128.9, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.3, 126.2, 43.1, 41.4, 21.5; IR (KBr) 1685, 1301, 1141 cm^{-1}; MS (EI) *m*/*z* (%) 465 (8.0, M^+ − PhSe), 309 (12.1, M^+ − PhSeH − SO_2Tol), 105 (100, $PhCO^+$). Anal. Calcd for $C_{36}H_{30}O_3SSe$: C, 69.56; H, 4.86. Found: C, 69.40; H, 4.98.

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Supporting Information Available: ^{1}H, and ^{13}C NMR spectra for compounds *Z*-**6a**−**t**, **9a**−**e**, **12a**−**f**, **14a**−**g**, *E*-**6c**, and *Z*-**4,** *E*-**4.** Experimental details, elemental analysis, and spectral data for all new compounds not described within the text, as well as the ORTEP figures of compounds *Z*-**4** and *Z*-**6f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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