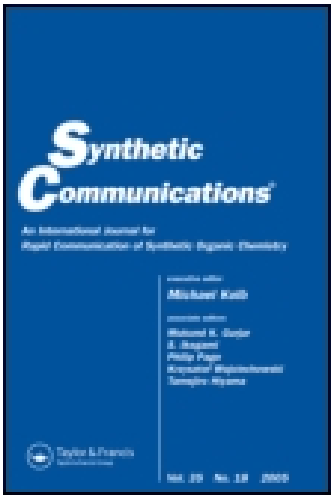

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One-Pot Stereoselective Synthesis of (*Z*)-1,2-Disubstituted Vinyl Sulfones by Hydrostannylation–Stille Tandem Reaction of Acetylenic Sulfones

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Abstract: (*Z*)-1,2-Disubstituted vinyl sulfones can be stereoselectively synthesized in one pot under mild conditions, in good yields, by the palladium-catalyzed hydrostannylation of acetylenic sulfones with tributyltin hydride, followed by Stille coupling with aryl iodides.

Keywords: Hydrostannylation, stereoselective synthesis, Stille coupling, tandem reaction, vinyl sulfone

INTRODUCTION

The stereoselective synthesis of polysubstituted alkenes remains a challenging problem in organic synthesis and is still being actively explored because of the fact that many biologically active compounds have the structural unit of polysubstituted alkenes.[1] Vinyl sulfones have served as a class of compounds of proven value in organic synthesis because of the reactivity offered by the sulfonyl functional group.[2–4] Thus, vinyl sulfones are excellent acceptors for Michael additions[5] and 2π partners in cycloaddition reaction.[6] In addition, alkylative desulfonylation has also provided a new strategy for stereospecific alkene synthesis.[7,8] A variety of methods have been developed for their preparation, including those

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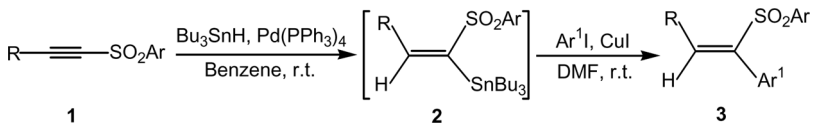
involving Horner–Emmons reactions of carbonyl compounds and sulfonyl phosphoranes,[9] Peterson reactions,[10] β-elimination of selenosulphones,[11] and selenosulfonation of acetylene.[12] An alternative convergent process involved the combination of a sulfone-stabilized carbanion with a carbonyl compound. In this regard, Knoevenagel condensation[13] and Horner–Wittig reaction[14] achieved great successes, and the (*E*)-vinyl sulfone was the exclusive product, but the preparation of the starting materials (such as sulfonomethyl-phosphonates) could be both inconvenient and time-consuming. In addition, protodesilylation of α-phenylsulfonyl allyl silanes also provided an indirect approach to vinyl sulfones.[15]

The stereoselective synthesis of polysubstituted vinyl sulfones is also of considerable interest in organic synthesis. Huang et al.[16] reported the synthesis of stereodefined *Z*-polysubstituted vinyl sulfones by hydrozirconation of acetylenic sulfones. Recently, Xie et al.[17,18] reported that polysubstituted vinyl sulfones could be synthesized by carbomagnesiation of acetylenic sulfones. Considering the importance of polysubstituted vinyl sulfones, it is still of interest to develop new routes for the synthesis of polysubstituted vinyl sulfones. Herein, we report that (*Z*)-1,2-disubstituted vinyl sulfones can be stereoselectively synthesized in one pot under mild conditions, in good yields, by the palladium-catalyzed hydrostannylation of acetylenic sulfones, followed by Stille coupling with aryl iodides.

RESULTS AND DISCUSSION

Recently, we found that the palladium-catalyzed hydrostannylation of acetylenic sulfones could proceed highly regio- and stereoselectively, affording (*E*)-α-stannylvinyl sulfones in high yields.[19] (*E*)-α-Stannylvinyl sulfones are new difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinylstannanes and as vinyl sulfones. Vinylstannanes can undergo the Stille coupling reaction with organic halides.[20–22] The tandem reaction has recently been of interest for organic synthesis because it offers a convenient and economical method by which to prepare target organic molecules.[23,24] The palladium-catalyzed hydrostannylation of alkynes and the Stille reaction are acknowledged as useful tools for constructing complex organic molecules. Considering the fact that both the hydrostannylation and Stille reaction were catalyzed by $Pd(PPh_3)_4$, we tried to combine the two reactions, in one pot, to stereoselectively prepare (*Z*)-1,2-disubstituted vinyl sulfones (Scheme 1).

We found that hydrostannylation of acetylenic sulfones **1** with tributyltin hydride using 5 mol% $Pd(PPh_3)_4$ in benzene, followed by solvent exchange (to dimethylformamide, DMF) and subsequent reaction with



Scheme 1. Synthesis of (Z)-1,2-disubstituted vinyl sulfones.

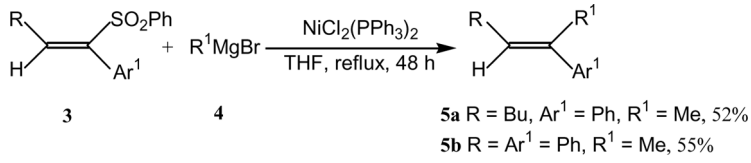
aryl iodides and 75 mol% copper iodide, gave the (*Z*)-1,2-disubstituted vinyl sulfones **3** in good yields. The typical results are summarized in Table 1. As shown in Table 1, the tandem hydrostannylation–Stille reaction of tributyltin hydride with a variety of acetylenic sulfones and aryl iodides proceeded smoothly, under very mild conditions, to afford the corresponding (*Z*)-1,2-disubstituted vinyl sulfones **3** stereoselectively. The nature of the substituents in aryl iodides has no influence on the Stille reaction. The Stille coupling reaction of the intermediates **2** with heteroaryl iodides and 1-iodonaphthalene also proceeded smoothly to give the corresponding coupled products in good yields (entries 7 and 8). However, when aryl bromides were used as the electrophiles, the Stille coupling reaction of the intermediates **2** did not occur at all.

Investigations of the crude products **3** by ^{1}HNMR spectroscopy (400 MHz) showed their isomeric purities by more than 98%. One olefinic proton signal of compounds **3a-c**, **3e**, **3f**, **3 h**, and **3j** splits characteristically into one triplet at $\delta = 6.11$–6.25 with coupling constant $J = 4.8$–7.6 Hz, which indicated that the hydrostannylation to acetylenic sulfones had taken place with strong preference for the addition of the tin atom at the carbon adjacent to the arylsulfonyl group. It is well documented that the Stille coupling reaction of vinylstannanes with organic halides,

Table 1. Synthesis of (*Z*)-1,2-disubstituted vinyl sulfones **3a–j**

Entry	R	Ar	Ar^1	Product	Yield[a] (%)
1	*n*-C_4H_9	Ph	Ph	**3a**	76
2	*n*-C_4H_9	Ph	4-$MeOCOC_6H_4$	**3b**	74
3	$MeOCH_2$	4-MeC_6H_4	4-MeC_6H_4	**3c**	70
4	Ph	Ph	Ph	**3d**	69
5	*n*-C_4H_9	4-MeC_6H_4	4-ClC_6H_4	**3e**	80
6	*n*-C_4H_9	4-MeC_6H_4	4-$O_2NC_6H_4$	**3f**	81
7	Ph	Ph	2-Thieny1	**3g**	79
8	*n*-C_4H_9	Ph	1-Naphthy1	**3h**	75
9	Ph	Ph	3-NCC_6H_4	**3i**	78
10	*n*-C_4H_9	4-MeC_6H_4	4-$MeOC_6H_4$	**3j**	76

[a]Isolated yield based on the aryl iodide used.



Scheme 2. Synthesis of stereodefined trisubstituted alkenes.

in the presence of a palladium catalyst, occurs with retention of configuration.[20,25] In addition, the *Z*-configuration of compound **3f** was confirmed by nuclear Overhauser effect spectroscopy (NOESY) experiments. An enhancement of the allylic protons was observed as the vinylic proton of **3f** was irradiated. A correlation between the allylic protons and the aromatic protons of (4-methylphenyl)sulfonyl group was observed. The NOE results indicate that compound **3f** has the expected *Z*-configuration and that the cross-coupling reaction of (*E*)-α-stannylvinyl sulfones with aryl iodides occurs with retention of configuration.

We have also carried out the cross-coupling reaction of compounds **3** with Grignard reagents in the presence of $NiCl_2(PPh_3)_2$ in THF to afford trisubstituted alkenes with high stereoselectivity in moderate yields (Scheme 2).

EXPERIMENTAL

General

Benzene was distilled from sodium immediately prior to use. DMF was dried by distillation over calcium hydride. IR spectra were obtained with a Perkin-Elmer 683 instrument as neat films. ^{1}H NMR spectra were recorded with a Bruker AC-400 (400-MHz) spectrometer using $CDCl_3$ as solvent. ^{13}CNMR spectra were recorded with a Bruker AC-400 (100-MHz) spectrometer using $CDCl_3$ as solvent. Mass spectra (EI) were determined with a Finnigan 8230 mass spectrometer. Microanalyses were measured with a Yanaco MT-3 CHN microelemental analyzer. $Pd(PPh_3)_4$ was prepared according to a literature procedure.[26] Acetylenic sulfones **1** were prepared by a literature method.[27]

General Procedure for the Synthesis of (*Z*)-1,2-Disubstituted Vinyl Sulfones 3a–j

A 25-mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar under an argon atmosphere was charged sequentially with

acetylenic sulfone **1** (1 mmol), benzene (4 mL), $Pd(PPh_3)_4$ (0.05 mmol), and Bu_3SnH (1.1 mmol). The mixture was stirred at room temperature for 4 h, the solvent was removed under reduced pressure, and the residue was dissolved in DMF (10 mL). Aryl iodide (0.9 mmol) and CuI (0.7 mmol) were added, and the mixture was stirred at room temperature for 8–12 h. The reaction mixture was diluted with Et_2O (30 mL), filtered, and then treated with 20% aqueous potassium fluoride (KF) (10 mL) for 30 min before the organic layer was dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether–Et_2O, 5:1).

Data

(*Z*)-1-Phenyl-1-phenylsulfonyl-1-hexene (**3a**)

Oil. IR (neat): ν (cm^{-1}) 3061, 2958, 2928, 1628, 1585, 1490, 1446, 1306, 1153, 1086, 760; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, $J = 7.6$ Hz, 2H), 7.54–7.37 (m, 3H), 7.28–7.17 (m, 5H), 6.18 (t, $J = 7.6$ Hz, 1H), 2.91–2.85 (m, 2H), 1.49–1.35 (m, 4H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 142.0, 141.1, 135.9, 133.0, 130.2, 128.7, 128.5, 128.0, 127.7, 31.5, 28.5, 22.4, 13.9; MS (EI): m/z 300 (M^+, 100), 196 (28), 117 (47). Anal. calc. for $C_{18}H_{20}SO_2$: C, 71.97; H, 6.71. Found: C, 72.23; H, 6.93%.

(*Z*)-1-(4-methoxycarbonylphenyl)-1-phenylsulfonyl-1-hexene (**3b**)

Oil. IR (neat): ν (cm^{-1}) 3066, 2956, 2927, 1717, 1607 1584, 1446, 1275, 1154, 1103, 1086, 772; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92–7.90 (m, 2H), 7.66–7.63 (m, 2H), 7.53–7.51 (m, 1H), 7.43–7.39 (m, 2H), 7.29–7.26 (m, 2H), 6.21 (t, $J = 7.6$ Hz, 1H), 3.91 (s, 3H), 2.93–2.87 (m, 2H), 1.52–1.38 (m, 4H), 0.95 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 147.8, 141.4, 140.8, 140.4, 133.3, 130.2, 130.1, 129.2, 128.9, 127.7, 52.2, 31.4, 28.5, 22.4, 13.9; MS (EI): m/z 359 ($M^+ + 1$, 100), 358 (M^+, 85), 217 (99), 115 (78); Anal. calc. for $C_{20}H_{22}SO_4$: C, 67.02; H, 6.19. Found: C, 66.84; H, 6.25%.

(*Z*)-1-(4-Methylphenyl)-1-(4-methylphenylsulfonyl)-3-methoxypropene (**3c**)

Oil. IR (neat): ν (cm^{-1}) 2957, 2925, 1643, 1595, 1510, 1314, 1148, 1112, 816, 696; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, $J = 8.4$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.4$ Hz, 2H), 7.04 (d, $J = 8.0$ Hz, 2H),

6.25 (t, $J = 4.8$ Hz, 1H), 4.77 (d, $J = 4.8$ Hz, 2H), 3.43 (s, 3H), 2.38 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 143.3, 141.2, 138.8, 137.1, 131.8, 129.7, 129.4, 128.8, 127.9, 69.8, 58.6, 21.6, 21.2; MS (EI): m/z 316 (M^+, 3.6), 269 (100), 267 (67), 91 (23). Anal. calc. for $C_{18}H_{20}SO_3$: C, 68.34; H, 6.37. Found: C, 68.15; H, 6.21%.

(*Z*)-1,2-Diphenyl-1-phenylsulfonylethene (**3d**)

White solid, mp 129–130°C (lit.,[28] 131°C). IR (KBr): ν (cm^{-1}) 3063, 2958, 2923, 1623, 1578, 1495, 1304, 1145, 1085, 776; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.24 (m, 15H), 7.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 141.5, 140.3, 135.8, 133.7, 132.9, 129.9, 129.4, 128.8, 128.7, 128.4, 128.2, 128.1, 127.8; MS (EI): m/z 320 (M^+, 56), 269 (23), 179 (100), 77 (31).

(*Z*)-1-(4-Chlorophenyl)-1-(4-methylphenylsulfonyl)-1-hexene (**3e**)

Oil. IR (neat): ν (cm^{-1}) 2957, 2926, 1629, 1596, 1487, 1456, 1319, 1152, 1087, 684; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, $J = 8.4$ Hz, 2H), 7.23–7.20 (m, 4H), 7.14–7.12 (m, 2H), 6.13 (t, $J = 7.6$ Hz, 1H), 2.89–2.84 (m, 2H), 2.39 (s, 3H), 1.48–1.32 (m, 4H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 144.2, 141.2, 138.0, 134.7, 134.5, 131.5, 129.5, 128.2, 127.7, 31.5, 28.5, 22.4, 21.6, 13.9; MS (EI): m/z 350 (M^+, ^{37}Cl, 21), 348 ($M^{+,}$ ^{35}Cl, 45), 151 (100), 91 (48). Anal. calc. for $C_{19}H_{21}SO_2Cl$: C, 65.40; H, 6.07. Found: C, 65.13; H, 5.88%.

(*Z*)-1-(4-Methylphenylsulfonyl)-1-(4-nitrophenyl)-1-hexene (**3f**)

Oil. IR (neat): ν (cm^{-1}) 3067, 2958, 2927, 1626, 1597, 1520, 1492, 1348, 1152, 1086, 814; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12–8.10 (m, 2H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.41–7.38 (m, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 6.22 (t, $J = 7.6$ Hz, 1H), 2.93–2.87 (m, 2H), 2.40 (s, 3H), 1.53–1.39 (m, 4H), 0.95 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 147.8, 144.6, 142.6, 140.8, 137.6, 131.1, 129.7, 127.7, 123.2, 31.3, 28.6, 22.5, 21.6, 13.9; MS (EI): m/z 359 (M^+, 52), 269 (100), 267 (87), 91 (56). Anal. calc. for $C_{19}H_{21}NSO_4$: C, 63.49; H, 5.89. Found: C, 63.21; H, 5.74%.

(*Z*)-2-Phenyl-1-phenylsulfonyl-1-(2-thienyl)ethene (**3g**)

White solid, mp 78–79°C. IR (KBr): ν (cm^{-1}) 3110, 1582, 1330, 1148, 1079, 728; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, $J = 8.0$ Hz, 2H), 7.48–7.40

(m, 4H), 7.35–7.30 (m, 7H), 7.00–6.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 140.4, 137.3, 136.1, 133.6, 133.1, 129.9, 129.4, 128.9, 128.6, 128.0, 127.9, 127.8, 127.2; MS (EI): m/z 326 (M^+, 2.2), 185 (56), 77 (100). Anal. calc. for $C_{18}H_{14}S_2O_2$: C, 66.23; H, 4.32. Found: C, 66.41; H, 4.55%.

(*Z*)-1-(1-Naphthyl)-1-phenylsulfonyl-1-hexene (**3h**)

Oil. IR (neat): ν (cm^{-1}) 3061, 2956, 2920, 1630, 1506, 1447, 1306, 1151, 1085, 803; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.60 (m, 5H), 7.44–7.18 (m, 7H), 6.24 (t, $J = 7.6$ Hz, 1H), 2.93–2.86 (m, 2H), 1.47–1.32 (m, 4H), 0.95 (t, $J =$ 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 140.4, 140.3, 133.4, 133. 1, 132.9, 132.7, 129.3, 129.1, 128.6, 128.2, 128.1, 126.4, 125.9, 125.5, 124.7, 31. 4, 28.6, 22.5, 14.0; MS (EI): m/z 350 (M^+, 1.2), 209 (92), 139 (93), 91 (100). Anal. calc. for $C_{22}H_{22}SO_2$: C, 75.39; H, 6.33. Found: C, 75.13; H, 6.44%.

(*Z*)-1-(3-Cyanophenyl)-2-phenyl-1-phenylsulfonylethene (**3i**)

White solid, mp 85–86°C. IR (KBr): ν (cm^{-1}) 3065, 2227, 1625, 1597, 1304, 1146, 1083, 749, 685; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.63 (m, 3H), 7.49–7.44 (m, 6H), 7.38–7.28 (m, 5H), 7.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 142.4, 139.7, 137.2, 134.4, 133.4, 133.3, 132.9, 132.3, 129.4, 129.3, 129.2, 128.7, 128.1, 128.0, 118.1, 112.7; MS (EI): m/z 345 (M^+, 17), 203 (100), 91 (26). Anal. calc. for $C_{21}H_{15}NSO_2$: C, 73.02; H, 4.38. Found: C, 72.75; H, 4.21%.

(*Z*)-1-(4-Methoxyphenyl)-1-(4-methylphenylsulfonyl)-1-hexene (**3j**)

Oil. IR (neat): ν (cm^{-1}) 2957, 2926, 1606, 1575, 1509, 1464, 1316, 1178, 1150, 688; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.13–7.11 (m, 2H), 6.78–6.76 (m, 2H), 6.11 (t, $J = 7.6$ Hz, 1H), 3.79 (s, 3H), 2.86–2.82 (m, 2H), 2.38 (s, 3H), 1.47–1.32 (m, 4H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 146.4, 143.8, 141.6, 138.3, 131.5, 129.4, 128.3, 127.7, 113.3, 55.3, 31.6, 28.5, 22.4, 21.6, 14.0; MS (EI): m/z 344 (M^+, 1.4), 209 (46), 178 (50), 165 (100), 91 (38). Anal. calc. for $C_{20}H_{24}SO_3$: C, 69.74; H, 7.02. Found: C, 69.51; H, 6.80%.

General Procedure for the Synthesis of Stereodefined Trisubstituted Alkenes 5a–b

To a stirred suspension of $NiCl_2(PPh_3)_2$ (0.05 mmol) and the (*Z*)-1,2-disubstituted vinyl sulfone **3** (1 mmol) in THF (6 mL), a 3.0 M THF solution

of MeMgBr (15 mmol) was added at room temperature under Ar. The mixture was stirred at reflux temperature for 48 h. After being cooled to room temperature, the mixture was quenched with sat. aq. NH_4Cl (15 mL) and extracted with Et_2O (2×30 mL). The organic layer was washed with water (3×10 mL) and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography on silica gel using light petroleum ether as eluent.

Data

(*E*)-2-phenylhept-2-ene[29] (**5a**)

Oil. IR (neat): ν (cm^{-1}) 3021, 2957, 2928, 1646, 1597, 851, 753; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37–7.10 (m, 5H), 5.71 (t, $J = 6.4$ Hz, 1H), 2.24–2.05 (m, 2H), 2.02 (s, 3H), 1.47–1.21 (m, 4H), 0.89 (t, $J = 7.2$ Hz, 3H). Anal. calc. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.31; H, 10.29%.

(*E*)-1-Methyl-1,2-diphenylethene[29] (**5b**)

Oil. IR (neat): ν (cm^{-1}) 3057, 2925, 1651, 1528, 1422; ^1H NMR (400 MHz, $CDCl_3$): δ 7.52–7.03 (m, 10H), 6.71 (m, 1H), 2.15 (d, $J = 1.3$ Hz, 3H). Anal. calc. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.52; H, 7.03%.

CONCLUSION

In conclusion, we have developed an efficient and stereoselective one-pot method for the synthesis of (*Z*)-1,2-disubstituted vinyl sulfones. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions, and good yields.

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