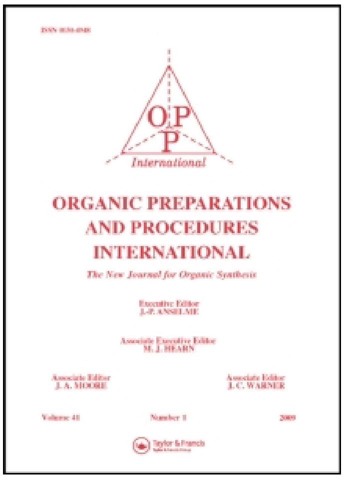

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OPPI BRIEFS

STEREOSELECTIVE SYNTHESIS OF (E)-VINYL ARYL SULFIDES *via* HYDROZIRCONATION OF TERMINAL ALKYNES

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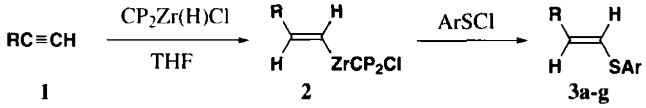
Vinyl sulfides have attracted special attention as important intermediates in various synthetic transformations,[1,2] and their stereospecific synthesis has been attempted.[3,4] However, no convenient synthesis of (E)-vinyl sulfides from aryl or alkyl substituted alkynes has been reported. For example, the addition of thiophenol to monosubstituted ethynes is very slow at room temperature and the products exhibit predominantly the Z configuration, or a mixture of the Z and E configurations.[5-7] It was reported that the palladium-catalyzed cross-coupling of 9-RS-9-BBN with (E)-1-iodo-1-alkenes afforded (E)-vinyl sulfides[8], but the synthesis of 9-RS-9-BBN and (E)-1-iodo-1-alkenes are not easy.

Vinylzirconium complexes reacted with phenyltellurenyl iodide or arylselenenyl bromides readily to afford (E)-vinyl tellurides[9] or (E)-vinyl selenides.[10] Considering the high electrophilicity of arylsulfenyl chloride, we decided to react them with the vinylzirconium complexes **2** produced by hydrozirconation of terminal alkyne **1**. The experimental results showed that the reaction proceeded easily to afford (E)-vinyl sulfides **3** whose configuration was confirmed by the coupling constants (J = 15-16 Hz) of the vinyl protons and the absorption bands at 945-960 cm^{-1} in IR spectrum.



1 **2** **3a-g**

The present method has advantages of high stereoselectivity, readily available starting materials, simple procedures and mild reaction conditions as well as high yields.

EXPERIMENTAL SECTION

^{1}H NMR spectra were recorded on PMX-60 spectrometer in CDCl$_3$ as the solvent with TMS as an internal standard. J values are given in Hz. IR spectra were determined as films on PE-683 spectrophotometer. Silica gel 60 GF254 was used for analytical and preparative TLC. All reactions were carried out in pre-dried glassware (140°, 4h) and cooled under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use. The arylsulfenyl chlorides were prepared from aryl thiols and sulfuryl chloride.[11]

TABLE. Synthesis of (E)-Vinyl Sulfides **3a-g**

Product	R	Ar	Yield(%)
3a	Ph	Ph	85
3b	Ph	4-MeC_6H_4	80
3c	Ph	4-ClC_6H_4	90
3d	*n*-Bu	Ph	86
3e	*n*-Bu	4-MeC_6H_4	74
3f	$AcOCH_2$	Ph	75
3g	CH_3OCH_2	Ph	88

General Procedure for the Synthesis of (E)-Vinyl Sulfides 3a-g.- A mixture of $Cp_2Zr(H)Cl$[12] (1mmol) and terminal alkyne **1** (1mmol) in THF (5mL) was stirred at room temperature for 20 min. The resulting solution was cooled to 0° and into it was injected ArSCl[11] (1mmol). Then the mixture was stirred at room temperature for 30 min. The solvent was removed on a rotary evaporator under reduced pressure. The residue was extracted with light petroleum (3 x 6 mL) and filtered through a short plug of silica gel. After evaporation of the filtrate, the residue was purified by preparative TLC on silica gel eluting with light petroleum.

Compound 3a: Colorless oil, lit.[13], bp. 150-151°/1.5mmHg, IR (film): 3040, 1612, 1594, 1470, 950, 688 cm^{-1}; ^{1}H NMR: δ 6.90-7.40 (m, 10H), 6.9 (d, 1H, J = 15), 6.65 (d, 1H, J = 15).

Anal. Calcd for $C_{14}H_{12}S$: C, 79.20; H, 5.70. Found: C, 78.98; H, 5.83

Compound 3b: Colorless oil, IR (film): 3070, 1610, 1580, 1505, 948, 775 , 689 cm^{-1}; ^{1}H NMR: δ 7.05-7.40 (m, 9H), 6.80 (d, 1H, J = 15), 6.60 (d, 1H, J = 15), 2.26 (S, 3H).

Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23. Found: C, 79.48; H, 6.35

Compound 3c: Colorless oil, lit.[13], bp. 164-165°/1.0mmHg, IR (film): 3050, 1608, 1580, 1480, 945, 810 cm^{-1}; ^{1}H NMR: δ 7.15-7.55 (m, 9H), 6.85 (d, 1H, J = 15), 6.56 (m, 1H).

Anal. Calcd for $C_{14}H_{11}ClS$: C, 68.15; H, 4.49. Found: C, 67.96 ; H, 4.56

Compound 3d: Colorless oil, IR (film): 3040, 1595, 1450, 955, 785 cm^{-1}; ^{1}H NMR: δ 7.00-7.50 (m, 5H), 6.05 (d, 1H, J = 15), 5.70 (m, 1H), 2.10 (m, 2H), 0.88-1.60 (m, 7H).

Anal. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39. Found: C,74.76; H,8.51

Compound 3e: Colorless oil, IR (film): 3040, 1500, 950,785 cm^{-1}; ^{1}H NMR: δ 6.90-7.40 (m, 4H), 6.05 (d, 1H, J = 15), 5.80 (m, 1H), 2.50 (s, 3H), 2.10 (m, 2H), 0.70-1.60 (m, 7H).

Anal. Calcd for $C_{13}H_{18}S$: C, 75.67; H, 8.79. Found: C,75.51; H, 8.93

Compound 3f: Colorless oil, IR (film): 3070, 1740, 1600, 1495, 955 cm^{-1}; ^{1}H NMR: δ 7.10-7.50 (m, 5H), 6.30 (d, 1H, J = 15), 5.70 (m, 1H), 4.45 (d, 2H, J = 6), 2.00 (s, 3H).

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81. Found: C, 63.28; H, 5.97

Compound 3g: Colorless oil, IR (film): 3080, 1595, 1488, 950 cm^{-1}; ^{1}H NMR: δ 7.00-7.50 (m, 5H), 6.30 (d, 1H, J = 15), 5.70 (m, 1H), 3.82 (d, 2H, J = 6), 3.20 (s , 3H).

Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71. Found: C, 66.40; H, 6.82

The ^{1}H NMR spectra of **3a**,[7] **3b**,[7] **3c**,[7] of **3d**,[6] **3e**[8] and of **3f**[14] and **3g**[14] were identical to those reported in the references cited.

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