SHORT PAPER

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Simple and stereoselective synthetic route to (*E*)-1-alkenyl sulfoxides via terminal alkynes†

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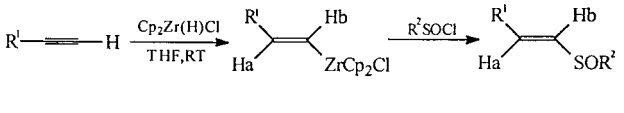
Terminal alkynes **1** react with $Cp_2Zr(H)Cl$ (Cp = η^5-C_5H_5) to give organozirconium (IV) complexes **2**, which are trapped with sulfuryl chloride to afford (*E*)-1-alkenyl sulfoxides **3**.

Unsaturated sulfoxides have been widely used as building blocks in organic chemistry, [1–3] but few convenient routes to such compounds are known.[4–7] For example, the Horner–Wittig procedure using carbonyl compounds and sulfinyl methylphosphonate anions leads to a mixture of (*E*)- and (*Z*)-l-alkenyl sulfoxides.[4] (*E*)- and (*Z*)-2-bromovinyl phenyl sulfoxides react with cuprates in a cross-coupling process giving the corresponding 1-alkenyl sulfoxides.[5] Reaction of 1-alkynyl *p*-tolyl sulfoxides with lithium aluminium hydride in THF at – 90 °C proceeds stereospecifically to give (*E*)-1-alkenyl sulfoxides.[6] (*E*)-1-Alkenylmagnesium bromides react with chiral menthyl sulfinate esters to produce chiral (*E*)-1-alkenyl sulfoxides.[7] But starting materials, such as (*E*)-2-bromovinyl phenyl sulfoxides and 1-alkynyl *p*-tolyl sulfoxides, are not easily available.

Recently, it was reported that alkenylzirconium(IV) complexes were transformed to other functional groups with a high level of stereochemical purity.[8] For example, vinylzirconium complexes react with phenyltellurenyl iodide, arylselenenyl bromides or acid chloride readily to afford (*E*)-vinyl tellurides,[9] (*E*)-vinyl selenides[10] or (*E*)-vinyl ketones[11] respectively. But the sulfoxidation of vinylzirconium complexes has not been reported. Considering the electrophilicity of sulfuryl chloride, we attempted to treat them with the vinylzirconium **2** produced by hydrozirconation of terminal alkynes **1**. Experimental results show that, $Cp_2Zr(H)Cl$[12] adds to terminal alkynes **1** in THF at room temperature stereospecifically with high regioselectivity to yield (*E*)-vinyl Zr(IV) complexes **2** which react with sulfuryl chloride at room temperature to afford (*E*)-1-alkenyl sulfoxides. The yields are good to excellent (see Table 1).



1 **2** **3**

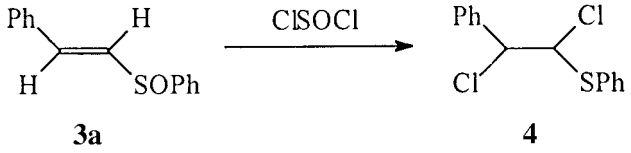
Scheme 1 R^1 = Ph, *n*-C_4H_9, *n*-C_5H_{11}; R^2 = Ph, 4-MeC_6H_4, $C_6H_4CH_2$

All the compounds **3** were purified by preparative TLC on silica gel and fully characterized by NMR spectroscopy. The ^{1}H NMR spectra of **3a**,[5] **3b**,[5] **3c**,[7] **3d**,[13] **3e**,[6] **3f**[6] and **3g**[14] were identical to those reported in the references cited. The stereochemistry of the vinyl sulfoxides was easily established, since ^{1}H NMR of products (**3a–g**) give rise to a doublet at 6.10–6.80 (H_b) with a coupling constant *ca* 16 Hz typical of *trans* positioned protons, while that of *cis* isomers give rise to a doublet (H_b) with a coupling constant *ca* 11 Hz.[5]

Table 1 Synthesis of compound **3a–g**

Product	R^1	R^2	M.p./C	Yield/%
3a	Ph	Ph	60–61 (61–62[6])	79
3b	*n*-C_4H_9	Ph	Oil	75
3c	*n*-C_5H_{11}	Ph	Oil	81
3d	Ph	4-MeC_6H_4	34–35 (34–35[15])	76
3e	*n*-C_4H_9	4-MeC_6H_4	Oil	84
3f	*n*-C_5H_{11}	4-MeC_6H_4	Oil	86
3g	Ph	$C_6H_5CH_2$	104–105(104–105[16])	74

Vinyl sulfoxides **3** have recently emerged as valuable reagents for organic synthesis. For example, **3a** was treated with 5 equivalents of thionyl chloride in methylene chloride at – 5 to 25 °C for 30 min to produce α, ß-dichlorosulfide **4** in 88 % yield (**Scheme 2**).[3]



3a **4**

Scheme 2

In conclusion, the hydrozirconation/sulfoxidation strategy provides a direct route to (*E*)-1-alkenyl sulfoxides from terminal alkynes. The method has some attractive advantages such as readily available starting materials, high yields, mild reaction conditions, straightforward access to exclusive (*E*)-configuration product and little pollution to environment.

Experimental

^{1}H NMR spectra were recorded on a AZ-300 spectrometer with TMS as internal standard. IR spectra were determined on PE-683 instrument as neat films. All reactions were carried out in pre-dried glassware (140 °C, 4h) and cooled under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use.

General procedure for the synthesis of **3a–g**. To a dry 10 ml flask containing $Cp_2Zr(H)Cl$ (1.2 mmol) was injected THF (5 ml), followed by the addition of terminal alkynes (1.2 mmol) at room temperature. The mixture was stirred for 20 min to yield a clear solution. Then sulfuryl chlorides (1.5 mmol were added), and stirred for 2 h. The solvent was removed using rotary evaporator under reduced pressure. The residue was extracted with light petroleum ether (3 × 6 ml) and filtered though a short plug of silica gel. After removal of solvent, the residue was purified by preparative TLC on silica gel eluting with hexane–AcOEt (95/5) to give **3**.

3a[5]: m.p. 60–61 °C (hexane/diethyl ether). IR (KBr): ν = 3080, 3040, 1610, 1590, 1485, 1445, 985, 920; ^{1}H NMR ($CDCl_3$): d = 7.70–7.30 (m, llH), 6.80 (d, *J* = 15.5 Hz, lH); Calc. For $C_{14}H_{12}OS$: C, 73.65; H, 5.30. Found: C, 73.44, H, 5.37%.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

3b[5]: oil. IR (film): ν = 3040, 1605, 1500, 1140, 970, 925; ^{1}H NMR ($CDCl_3$): δ = 7.60–7.10 (m, 5H), 6.40 (dt, *J* = 15 and 6 Hz, 1H), 6.10 (d, *J* = 15Hz, 1H), 2.35–2.00 (m, 2H), 1.65–1.15 (m, 4H), 0.92 (br t, *J* = 6Hz, 3H); Calc. For $C_{12}H_{16}OS$: C, 69.19; H, 7.74. Found: C, 69.45, H, 7.79%.

3c[7]: oil. IR (film): ν = 3060, 2940, 2878, 1600, 1500, 1076, 1040; 940; ^{1}H NMR ($CDCl_3$): δ = 7.60–7.10 (m, 5H), 6.45 (dt, *J* = 15.5 and 6.5 Hz, 1H), 6.13 (d, *J* = 15.5 Hz, 1H), 2.40–2.00 (m, 2H) 1.65–1.15 (m, 6H), 0.93 (br t, *J* = 6Hz, 3H); Calc. for $C_{13}H_{18}OS$: C, 70.22; H, 8.16. Found: C, 70.02, H, 8.12%.

3d[13]: m.p. 34–35 °C (hexane/diethyl ether). IR (film): ν = 3055, 2990, 2940, 2880, 1610, 1500, 1088, 1040, 970; ^{1}H NMR ($CDCl_3$): δ = 7.80–7.00 (m, 10H), 6.73 (d, *J* = 15.5, 1H), 2.35 (s, 3H); Calc. for $C_{15}H_{14}OS$: C, 74.34; H, 5.82. Found: C, 74.98, H, 5.80 %.

3e[6]: oil. IR (film): ν = 3040, 2980, 2950, 2890, 1645, 1600, 1500, 1085, 1040; ^{1}H NMR ($CDCl_3$): δ = 7.50–7.10 (AB q, *J* = 8 Hz, 4H), 6.40 (dt, *J* = 15.5 and 6 Hz, 1H), 6.10 (d, *J* = 15.5 Hz, 1H), 2.38 (s, 3H), 2.35–1.95 (m, 2 H), 1.60–1.10 (m, 4H), 0.90 (br t, *J* = 6 Hz, 3H); Calc. for $C_{13}H_{18}OS$: C, 70.22; H, 8.16. Found C, 70.33, H, 8.08%.

3f[6]: oil. IR (film): ν = 3060, 2980, 2880, 1635, 1605, 1495, 1090, 1035; ^{1}H NMR ($CDCl_3$) δ = 7.70–7.15 (AB q, *J* = 8 Hz, 4H), 6.50 (dt, *J* = 15.5 and 6 Hz, 1H), 6.20 (d, *J* = 15.5 Hz, 1H), 2.40 (s, 3H), 2.40–2.00 (m, 2 H), 1.80–1.10 (m, 6H), 0.88 (br t, *J* = 6 Hz, 3H); Calc. for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; Found C, 71.26, H, 8.46 %.

3g[14]: m.p. 104–105 °C (methanol). IR (film): ν = 3080, 1600, 1595, 1490, 1445, 980, 920; ^{1}H NMR ($CDCl_3$) δ = 7.40–7.10 (m, 10H), 7.07 (d, *J* = 15.5 Hz, 1H), 6.70 (d, *J* = 15.5 Hz, 1H), 4.05 (s, 2H); Calc. for $C_{15}H_{14}OS$: C, 74.34; H, 5.82. Found: C, 74.49, H, 5.76%.

Synthesis of α, ß-dichlorosulfide 4°. Thionyl chloride (10 mmol) in methylene chloride (3 ml) were added to a methylene choride (5 ml) solution of **3a** (2 mmol) at –5 °C. The mixture was stirred at –5 – 25 °C for 30 min. The workup gave 88 % α, β-dichlorosulfide **4**, which was purified by flash chromatography (hexane–AcOEt 95/5).

4. oil. IR (film): ν = 3085, 2945, 2880, 1595, 1480, 1150, 1080, 1040; ^{1}H NMR ($CDCl_3$): δ = 7.60–7.00 (m, 10H), 5.35 (d, *J* = 6 Hz, 1H), 5.07 (d, *J* = 6 Hz, 1H); Calc. for $C_{14}H_{12}Cl_2S$: C, 59.37; H, 4.27. Found: C, 59.70, H, 4.19%.

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