J. Serb. Chem. Soc. 69(3)175–178(2004)
JSCS – 3142

UDC 678.745+542.913
Original scientific paper

Stereoselective synthesis of (*E*)-vinyl alkyl sulfides *via* hydrozirconation of terminal alkynes

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(Received 15 July, revised 3 November 2003)

Abstract: Terminal alkynes react with $Cp_2Zr(H)Cl$ (Cp = η^5-C_5H_5) to give organozirconium complexes, which are trapped with alkylsulfenyl chlorides to afford (*E*)-vinyl alkyl sulfides in good yield.

Keywords: alkyne, sulfide, alkylsulfenyl chloride, hydrozirconation, synthesis.

INTRODUCTION

Vinyl sulfides have attracted special attention as important intermediates in various synthetic transformations,[1,2] and their stereospecific synthesis has been attempted.[3,4] To our knowledge, there are only a few stereoselective syntheses of 1-alkenyl sulfides reported. These methods include the reduction of vinyl sulfoxides by EtMgBr/CI,[5] the cross-coupling reaction of 1-alkenyl halides with metal thioalkoxides in the presence of a transition-metal catalyst,[6] as well as the reaction of β-sulfinium vinyl boron compounds with catecholborane cross-coupling on organic halides[7] in the presence of the catalyst $PdCl_2$(dppf). The two first methods require stereodefined vinylsulfoxides and vinyl halides, which cannot always be obtained with high stereo-selectivity. The corresponding vinyl halides are also needed in the third one with a phase-transfer catalyst and a longer reaction time. A convenient stereoselecitve method for the synthesis of (*E*)-vinyl sulfides will be described in this paper.

Hydrozirconation of alk-1-ynes in THF at room temperature gave with high stereo- and regioselectivity vinylzirconium compounds, which, considering their high electrophilicity, were reacted with arylsulfenyl chlorides.[8] The vinylzirconium compounds could also react with disulfides to afford (*E*)-vinyl sulfides at 60 ºC.[9] Now the reactivity of alkylsulfenyl chlorides with vinyl zirconium compounds were studied. The experimental results showed that the reactions occur at room temperature to afford (*E*)-vinyl alkyl sulfides in good yields.

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EXPERIMENTAL

General

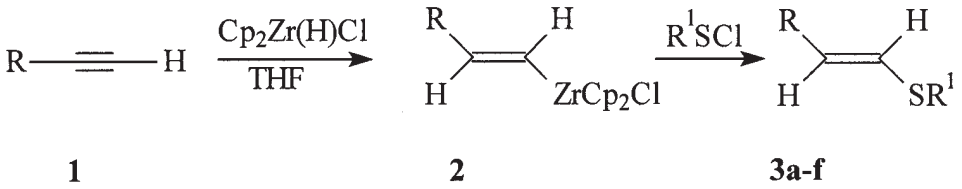
^{1}H (200 MHz) NMR spectra were recorded on a Bruker AC-300 spectrometer in $CDCl_3$ as the solvent with TMS as the internal standard. IR spectra were determined as films on a PE-683 spectrophotometer. Mass spectra were obtained on a Finnigan Mat 8230 spectrometer (EI, 70 eV). All reactions were carried out in pre-dried glassware (140 ºC, 4 h and cooled under a stream of dry nitrogen). All solvents were dried, deoxygenated and redistilled before use.

*General procedure for the synthesis of **3a-f***

A mixture of $Cp_2Zr(H)Cl$[10] (1 mmol) and a terminal alkyne **1** (1 mmol) in THF (5 ml) was stirred at room temperature for 20 min. The resulting solution was cooled to 0 ºC and freshly prepared R^1SCl[11] (1 mmol) was injected into it. Then the mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure. The residue was extracted with light petroleum (3 × 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 using light petroleum as eluent.

RESULTS AND DISCUSSION

As described in the Experimental section, terminal alkynes **1** react with $Cp_2Zr(H)Cl$ ($Cp = \eta^5$-C_5H_5) to give organozirconium complexes **2**, due to the steric crowding around the zirconium atom, which are stereoselectively trapped with alkylsulfenyl chlorides to afford (*E*)-vinyl alkyl sulfides **3** in good yield.



Scheme 1.

The results of the reaction are summarized in Table I. Freshly prepared R^1SCl had to be used for the reaction, otherwise the reaction hardly took place.

TABLE I. Synthesis of (*E*)-vinyl alkyl sulfides **3a-f**

Product	R	R^1	Yield*/%
3a	Ph	$PhCH_2$	80
3b	*n*-Bu	$PhCH_2$	73
3c	Ph	*n*-Bu	84
3d	*n*-Bu	*n*-Bu	77
3e	Ph	CH_3	79
3f	4-MeC_6H_4	CH_3	81

*Isolated yield

All the compounds **3** were fully characterized by ^{1}H-NMR, MS and IR spectroscopy. The ^{1}H-NMR spectra of **3a**,[12] **3b**,[12] **3c**,[13] **3d**,[14] **3e**[14] and **3f**[14] were iden-

tical to those reported in the references. The *E* configuration of the products was established *via* the coupling constants (J = 15–16 Hz) of the vinyl protons.

(E)-*[[(2-Phenylethenyl)thio]methyl]benzene* (**3a**). Oil. IR (film): 3080, 1622, 1600, 1450, 940, 685 cm^{-1}; ^{1}H-NMR: δ 7.20–7,50 (*m*, 11H), 6.65 (*d*, 1H, J = 15.5) 3.95 (*s*, 2H); *m*/*z* (EI): 226 (M^+), 135 ($M^+ - CH_2Ph$), 91 (CH_2Ph). Anal: Calcd. for $C_{15}H_{14}S$: C, 79.60; H, 6.23. Found: C, 79.98; H, 6.33.

(E)-*[(1-Hexenylthio)methyl]benzene* (**3b**). Oil. IR (film): 3060, 1505, 1458, 950, 870, 785, 695 cm^{-1}; ^{1}H-NMR: δ 7.20–7.40 (*m*, 5H), 5.95 (*d*, 1H, J = 15), 5.70 (1H, A part of an ABX_2 system, J_{AB} = 15, J_{AX} = 6.5), 3.90 (*s*, 2H), 2.0–2.2 (*m*, 2H), 1.2–1.4 (*m*, 4H), 0.9 (*m*, 3H); *m*/*z* (EI): 206 (M^+), 115 ($M^+ - CH_2Ph$), 91 (CH_2Ph). Anal: Calcd. for $C_{13}H_{18}S$: C, 75.67; H, 8.79. Found: C, 75.48; H, 8.85.

(E)-*[2-(Butylthio)ethenyl]benzene* (**3c**). Oil. IR (film): 3026, 2940, 2880, 1610, 1500, 1455, 940, 780, 730, 695 cm^{-1}; ^{1}H-NMR: δ 7.15–7.65 (*m*, 5H), 6.85 (*d*, 1H, J = 16), 6.55 (*d*, 1H, J = 16), 2.80 (*t*, 2H, J = 7.0), 1.20–1.70 (*m*, 4H), 1.0 (*t*, 3H, J = 5); *m*/*z* (EI): 192 (M^+), 135 ($M^+ - C_4H_9$). Anal: Calcd. for $C_{12}H_{16}S$: C, 74.94; H, 8.39. Found: C, 74.86; H, 8.56.

(E)-*1-(Butylthio)-1-hexene* (**3d**). Oil. IR (film): 3015, 1590, 1450, 950, 790 cm^{-1}; ^{1}H-NMR: δ 5.90 (*d*, 1H, J = 15), 5.80 (*m*, 1H), 2.70 (*t*, 2H, J = 6.5), 2.30 (*t*, 2H, J = 6.5), 1.54 (*m*, 4H), 1.35 (*m*, 4H), 0.95 (*m*, 3H), 0.83 (*m*, 3H); *m*/*z* (EI): 172 (M^+), 115 ($M^+ - C_4H_9$). Anal: Calcd. for $C_{10}H_{20}S$: C, 69.70; H, 11.70. Found: C, 69.58; H, 11.65.

(E)-*[2-(Methylthio)ethenyl]benzene* (**3e**). Oil. IR (film): 1590, 1515, 910, 845, 760, 690, 520 cm^{-1}; ^{1}H-NMR: δ 7.20–7.60 (*m*, 6H), 6.35 (*d*, 1H, J = 15.5), 2.30 (*s*, 3H); *m*/*z* (EI): 150 (M^+), 135 ($M^+ - CH_3$). Anal: Calcd. for $C_9H_{10}S$: C, 71.95; H, 6.71. Found: C, 71.68; H, 6.79.

(E)-*1-Methyl-4-[2-(methylthio)ethenyl]benzene* (**3f**). Oil. IR (film): 1600, 1515, 820, 680, 525 cm^{-1}; ^{1}H-NMR: δ 7.10–7.50 (*m*, 4H), 6.70 (*d*, 1H, J = 15.5), 6.30 (*d*, J = 15.5), 2.25 (*s*, 3H); *m*/*z* (EI): 164 (M^+), 149 ($M^+ - C_4H_9$). Anal: Calcd. for $C_{10}H_{12}S$: C, 73.12; H, 7.36. Found: C, 73.29; H, 7.42.

CONCLUSION

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

Acknowledgement: This work was supported by the National Nature Science Foundation of China (No. 20272043) and the Nature Science Foundation of Zhejiang Province (No. 201015).

ИЗВОД

СТЕРЕОСЕЛЕКТИВНА СИНТЕЗА (*E*)-ВИНИЛ–АЛКИЛ–СУЛФИДА ХИДРОЦИРКОНОВАЊЕМ ТЕРМИНАЛНИХ АЛКИНА

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Терминални алкини реагују са $Cp_2Zr(H)Cl$ ($Cp = \eta^5\text{-}C_5H_5$) стварајући органоцирконијумове комплексе који су преведени са алкилсулфенил–хлоридима у (*E*)-винил–алкил–сулфиде уз добар принос.

(Примљено 11. јула 2003)

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