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Stereo-recognizing transformation of (*E*)-alkenyl halides into sulfides catalyzed by nickel(0) triethyl phosphite complex

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Abstract—(*E*)-Alkenyl halides were transformed into (*E*)-alkenyl sulfides by the nickel(0) triethyl phosphite complex-catalyzed reaction with thiols, whereas (*Z*)-alkenyl halides gave alkynes under the same reaction conditions. Aryl halides were also transformed into aryl sulfides using the same reagent system.

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1. Introduction

Alkenyl sulfides are useful synthetic intermediates and are employed as precursors for acyl anion equivalents,¹ equivalents of enolates,² Michael acceptors,³ components of [2+2] cycloadditions,⁴ and synthetic intermediates for certain cyclic compounds.⁵ Among various methods for their preparations, the transition metal-catalyzed transformation of alkenyl halides or triflates into alkenyl sulfides has attracted much attention in recent years. A variety of palladium(0) complexes have been found to serve as effective catalysts.⁶ Transformation of alkenyl halides into sulfides using a stoichiometric⁷ or a catalytic⁸ amount of copper(I) complexes has also been reported. Alkenyl sulfides are obtained by the σ -aryl-Ni[PPh₃]₂Cl-catalyzed reaction of alkenyl halides with thiols under phase transfer conditions.^{6b} Bis(bipyridine)nickel(II) bromide also catalyzes the transformation though rather drastic conditions are indispensable.⁹

In connection with our study on the titanocene(II)-promoted reaction of alkenyl sulfones with unsaturated compounds,¹⁰ we required a practical method for the stereoselective preparation of disubstituted alkenyl sulfides from alkenyl halides. Despite the above extensive studies, a little has been known about the stereochemistry of the transformation.⁸ The foregoing reactions catalyzed by transition metals require rather high reaction temperature and long reaction time. The catalysts used in these reactions are either expensive or difficult to be handled in an uncontrolled environment. Then we explored an alternative practical method

for the stereoselective transformation of alkenyl halides into sulfides using a less expensive and air-stable catalyst and found that nickel(0) triethyl phosphite complex **1**¹¹ was extremely effective for the conversion. The nickel catalyst **1** is easily prepared by the treatment of nickel(II) chloride with triethyl phosphite and is stable in air.

2. Results and discussion

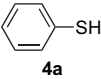
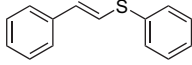
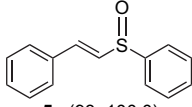
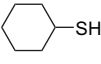
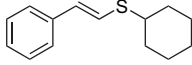

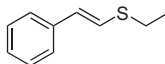
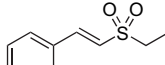

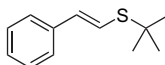
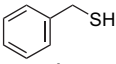
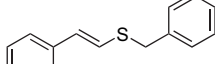
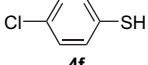
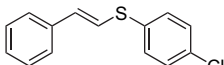
The treatment of β -bromostyrene **2a** (*E/Z*=85:15–90:10) with benzenethiol **4a** (1.2 equiv) at 120 °C in the presence of **1** (5 mol %) and triethylamine (2 equiv) in DMF produced β -(phenylthio)styrene **3a** in 90% yield (Table 1, entry 1). The decrease in the yield of **3a** was observed when the reaction was carried out at lower temperature (50 °C) (entry 2). The quantitative formation of **3a** was achieved by the reaction using *N,N*-diethylaniline (2.0 equiv) as a base at 70 °C (entry 3). The alkenyl sulfide **3a** was obtained in satisfactory yield using 1.5 equiv of *N,N*-diethylaniline even at 50 °C (entry 4). On the contrary, the reaction of **2a** with cyclohexanethiol **4b** under the same reaction conditions gave no alkenyl sulfide. To increase the nucleophilicity of the alkanethiol **4b**, sodium hydride was used as a base, and the alkenyl sulfide **3b** was obtained in 44% yield along with 40% recovery of the starting material (entry 6). Lengthening of reaction time gave a similar result, but the starting material was completely consumed in a short period of time by the use of THF as a co-solvent to produce **3b** in good yield (entry 7) (Scheme 1).

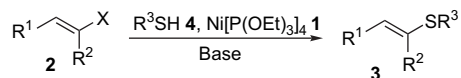
The alkenyl sulfides **3** obtained by the reaction of β -bromostyrene **2a** were the mixtures of stereoisomers with predominance of *E*-configuration. We considered the possibility that

Keywords: Cross coupling; Nickel(0) complexes; Thiols; Sulfides.

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Table 1. Reaction of β -bromostyrene **2a**^a with thiols **4**

Entry	Thiol 4	Base (equiv)	Solvent	Temp (°C)	Time (h)	Product (yield/% ^b ratio of stereoisomers)
1	 4a	Et ₃ N (2.0)	DMF	120	23	 3a (90, 93:7)
2	4a	Et ₃ N (2.0)	DMF	50	23	3a (53, 99:1)
3	4a	PhNEt ₂ (2.0)	DMF	70	23	3a (98, 89:11)
4	4a	PhNEt ₂ (1.5)	DMF	50	24	3a (88, 89:11)
5 ^c	4a	PhNEt ₂ (1.5)	DMF	50	24	 5a (93, 100:0)
6	 4b	NaH (1.5)	DMF	50	24	 3b (44, 88:12)
7	4b	NaH (1.5)	DMF/THF	50	2.5	3b (93, 88:12)
8	 4c	NaH (1.5)	DMF/THF	50	2.5	 3c (91, 91:9)
9 ^c	4c	NaH (1.5)	DMF/THF	50	2.5	 6 (78, 100:0)
10	 4d	NaH (1.5)	DMF/THF	50	2.5	 3d (95, 90:10)
11	 4e	NaH (1.5)	DMF/THF	50	8	 3e (90, 90:10)
12	 4f	NaH (1.5)	DMF/THF	50	4	 3f (85, 87:13)

^a *E/Z*=85:15–90:10.^b Isolated yield.^c The alkenyl sulfide **3** was oxidized with MCPBA in the same vessel without any isolation or purification.**Scheme 1.** Formation of alkenyl sulfides by the reaction of alkenyl halides with thiols.

the concomitant formation of *Z*-alkenyl sulfides was due to the photoisomerization of the *E*-isomers during and after isolation, since such isomerization has been known.¹² Then the reactions of **2a** with **4a** and **4c** were performed in the dark, and a dichloromethane solution of *m*-chloroperbenzoic acid (MCPBA) (10 equiv) was added to the mixtures to oxidize the resulting alkenyl sulfides **3a** and **3c**. The sulfoxide **5a** formed from the reaction with **4a** and the sulfone **5b** formed from that with **4c** were single isomers with *E*-configuration (entries 5 and 9).¹³ These facts indicate that the reaction is stereoselective. If the reaction is stereospecific, it is

undeniable that (*Z*)- β -bromostyrene **2a** isomerizes to the *E*-isomer under the reaction conditions; such isomerization explains the excess formation of *E*-isomers over theoretical amount estimated by the ratio of stereoisomers of the starting material **2a**.

The reactions of (*E*)-1-alkenyl halides **2** and thiols **4** also gave (*E*)-alkenyl sulfides **3** in high yields (Table 2). Although the reaction of **2a** with **4a** gave the alkenyl sulfide **3g** as a mixture of stereoisomers, the corresponding sulfoxide **5b** was obtained as a single stereoisomer by the reaction in the dark and subsequent oxidation. What is striking is that the reaction of (*Z*)-**2c** with 2-methyl-2-propanethiol **4d** gave no alkenyl sulfide but the alkyne **7a** was selectively produced (entry 6). The elimination also took place in the absence of the thiol **4d**. The result marks a sharp contrast with the conventional transition metal-catalyzed transformations.^{6a,8}

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