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# Cross-coupling of (*Z*)-1,2-bis(ethylseleno)ethene with the Grignard reagents

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## Abstract

The nickel-catalyzed cross-coupling of (*Z*)-1,2-bis(ethylseleno)ethene with the alkyl magnesium bromides proceeds with substitution of both ethylseleno groups to afford symmetrical alkenes, (*Z*)-RCH=CHR, in high yield with complete retention of configuration. In the case of phenyl magnesium bromide the monoarylation occurs to form (*Z*)-2-ethylseleno styrene, EtSeCH=CHPh.

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**Keywords:** *cis*-Alkenes; 1,2-Bis(ethylseleno)ethene; Cross-coupling; Nickel; Selenide

## 1. Introduction

The addition of compounds bearing the element–element bond to alkynes [1,2] followed by the substitution of an organoelement group by an organyl moiety via cross-coupling constitutes a promising synthetic approach to substituted olefins. Cross-coupling of the Grignard reagents with alkenyl halides [3,4], sulfides [5–8], selenides [9] and tellurides [10] catalyzed with the Ni(II) complexes such as NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, NiCl<sub>2</sub>(dppp) is a promising method to prepare substituted olefins with complete retention of the configuration. The reaction of the Grignard reagents with 1,1- and 1,2-dichloroethenes [3,4] most easily proceeds in a case of aryl magnesium bromides. With the alkyl Grignard reagents the reaction proceeds reluctantly to form mainly homo-coupling products. Though according to the paper [3], the Ni-catalyzed diarylation of (*E*)-1,2-dichloroethene proceeds with complete retention of the configuration, Japanese authors [4] have found that under the NiCl<sub>2</sub>(dppe) catalysis both (*Z*)- and (*E*)-1,2-dichloroethenes give mixtures of (*Z*)- and (*E*)-stilbenes. In general, authors

[4] consider the method for preparation of substituted olefins from 1,2-dichloroethenes to be rather restricted due to the formation of complicated mixtures.

## 2. Results and discussion

Previously we have studied the addition of organic diselenides to alkynes under radical [11], base-catalyzed [12], and palladium-catalyzed [13] conditions to afford 1,2-bis(organylseleno)ethenes. Since the cross-coupling reaction of the Grignard reagents with bis(organylseleno)ethenes was unknown, and it was not clear whether both organylseleno groups could be substituted we studied the Ni-catalyzed cross-coupling of (*Z*)-1,2-bis(ethylseleno)ethene (**1**) with aryl- and alkyl magnesium bromides (**2a–d**). It is known [8] that the cross-coupling reaction of alkenyl aryl selenides requires 2 mol of the Grignard reagent per 1 mol of the selenide and the cleavage of the C–Se bond takes place at both sides of the selenium atom. Taking this into account, we used 4 mol of the Grignard reagent for diarylation and dialkylation of 1 mol of the ethene **1**.

We have found that the reaction with alkyl magnesium bromides proceeds with substitution of both

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ethylseleno groups to afford symmetrical alkenes **3a–c** in high yield (Table 1) with complete retention of the configuration. In the case of the aromatic Grignard reagents, phenyl magnesium bromide, only monoarylation takes place under similar conditions (Scheme 1).

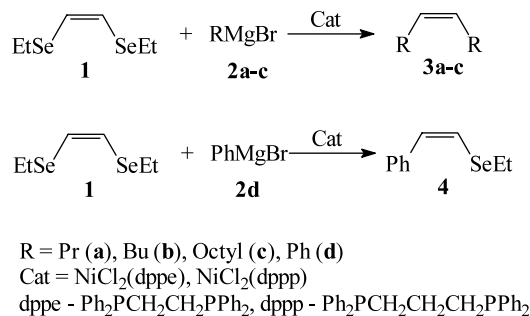
The structural assignment of ethenes **3a–c** was established by MS,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR. The (*Z*)-configuration of the alkenes **3a–c** was unambiguously determined by the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra, which are identical to those of the known (*Z*)-alkenes [14–21].

The replacement of  $\text{NiCl}_2(\text{dppe})$  by  $\text{NiCl}_2(\text{dppp})$ , the catalyst with the more lengthy carbon chain, seems to have little influence on the yield of products. When we used  $\text{NiCl}_2(\text{dppp})$  instead of  $\text{NiCl}_2(\text{dppe})$  in the reaction of butyl magnesium bromide with the ethene **1**, an insufficient increasing the yield of **3b** was observed (from 71 to 78%). Under these conditions (*Z*)-ethyl-1-hexen-1-yl selenide (**5**) was formed in low yield (11%) along with the symmetrical ethene **3b**. Its presence in the reaction mixture was established by the GC–MS and  $^1\text{H}$ -NMR spectroscopy. The coupling constant value of vinylic protons (9 Hz) pointed to (*Z*)-configuration of the selenide **5**.

The formation of (*Z*)-2-ethylseleno styrene (**4**) in the reaction of the ethene **1** with phenyl magnesium bromide was indicated by GC–MS data and by identity of its  $^1\text{H}$ -NMR spectrum to that of an authentic sample prepared by addition of ethylselenolate anion to phenylacetylene [22]. The coupling constant value for vinylic protons (10 Hz) in the styrene **4** corresponding to the (*Z*)-structure [22–24] points to retention of configuration of the parent ethene **1** on arylation.

Besides ethenes **3a–c**, **4**, **5**, some alkanes and alcohols were detected in the reaction mixture. These compounds seem to be a result of monocoupling reactions and hydrolysis. Formation of 1-phenylethanol  $\text{PhCH}(\text{OH})\text{CH}_3$  determined by mass spectrometry and  $^1\text{H}$ -NMR spectrometry speaks in favor of the formation of  $\text{PhCH}=\text{CHMgBr}$  giving on hydrolysis styrene  $\text{PhCH}=\text{CH}_2$  and then 1-phenylethanol.

Thus, the Ni-catalyzed cross-coupling of the Grignard reagents with the ethene **1** proceeds with complete retention of configuration as the dialkylation process



Scheme 1.

with alkyl magnesium bromides and as the monoarylation process with phenyl magnesium bromide.

### 3. Experimental

(*Z*)-1,2-Bis(ethylseleno)ethene (**1**) was prepared by the method [12].  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker DPX-400 spectrometer. Chromatograms were obtained on a HP 5971A spectrometer (70 eV).

#### 3.1. The $\text{NiCl}_2(\text{dppe})$ -catalyzed cross-coupling of (*Z*)-1,2-bis(ethylseleno)ethene (**1**) with *n*-octyl magnesium bromide (**2c**)

To a solution of the ethene **1** (244 mg, 1 mM) and  $\text{NiCl}_2(\text{dppe})$  (54 mg, 0.1 mM) in 4 ml of  $\text{Et}_2\text{O}$  were added 5 ml of the 0.8 N ether solution of octyl magnesium bromide (**2c**) (4 mM) under nitrogen atmosphere and the mixture was stirred for 9 h at room temperature till finishing of the reaction (disappearance of the ethene **1** peak in the GC). The mixture was treated with 0.2 N HCl solution, extracted with  $\text{Et}_2\text{O}$ , the ether extracts were dried over  $\text{MgSO}_4$ . The solvent and low boiling products were removed in vacuo. According to the GC–MS data the residue contains **3c** (214 mg, 85% yield), hexadecane (115 mg) and decane (56 mg). Separation of the mixture was performed by column chromatography (silicagel L5/40, eluents: successively hexane,  $\text{CHCl}_3$  and acetone).

Table 1  
The yields and  $^1\text{H}$ -NMR data <sup>a</sup> of the ethenes **3a–c**

Compound	Yield (%)	$^1\text{H}$ -NMR data, ppm ( $^3J_{\text{HH}}$ , Hz)			
		=CH	( $\text{CH}_2$ ) <sub>z</sub>	( $\text{CH}_2$ ) <sub>n</sub>	$\text{CH}_3$
<b>3a</b>	80 <sup>b</sup>	5.34 t (7)	1.99 dt (7)	1.16 m	0.91 t (7)
<b>3b</b>	71 <sup>b</sup> , 78 <sup>c</sup>	5.33 t (5)	2.00 dt (6)	1.25 m	0.90 t (6)
<b>3c</b>	85 <sup>b</sup>	5.34 t (5)	2.01 dt (7)	1.25 s	0.87 t (7)

<sup>a</sup> In  $\text{CDCl}_3$ , chemical shifts ( $\delta$ ) in ppm ( $\pm 0.01$ ) to high frequency of  $\text{SiMe}_4$ . s, singlet; t, triplet; dt, doublet of triplets; m, multiplet.

<sup>b</sup> With  $\text{NiCl}_2(\text{dppe})$ .

<sup>c</sup> With  $\text{NiCl}_2(\text{dppp})$ .

3.2. *The NiCl<sub>2</sub>(dppp)-catalyzed cross-coupling of (Z)-1,2-bis(ethylseleno)ethene (1) with n-butyl magnesium bromide (2b)*

Analogously to the procedure described for **2c**, the ethene **1** (484 mg, 2 mM), NiCl<sub>2</sub>(dppp) (111 mg, 0.2 mM), and 8.4 ml of the 0.95 N ether solution of butyl magnesium bromide (**2b**) (8 mM) were reacted. The residue after the evaporation in vacuo contains according to the GC–MS **3b** (219 mg, 78% yield), (Z)-EtSeCH=CHBu (42 mg, 11% yield), 1-butanol (41 mg), *n*-octane (226 mg) and EtSeSeEt (145 mg). Separation of the mixture was performed by column chromatography (silicagel L5/40, eluents: successively hexane, CHCl<sub>3</sub> and acetone).

3.3. *The NiCl<sub>2</sub>(dppe)-catalyzed cross-coupling of (Z)-1,2-bis(ethylseleno)ethene (1) with phenyl magnesium bromide (2d)*

Analogously to the procedure described for **2c**, the ethene **1** (484 mg, 2 mM), NiCl<sub>2</sub>(dppe) (54 mg, 0.1 mM), and 10 ml of the 0.92 N ether solution of phenyl magnesium bromide (**2d**) (9.2 mM) were reacted. The residue after the evaporation in vacuo contains according to the GC–MS unconverted **1** (89 mg, 82% conversion), 2-ethylseleno styrene (**4**) (73% yield on the ethene **1** reacted), diphenyl (186 mg) and 1-phenylethanol (93 mg). Separation of the mixture was performed by column chromatography (silicagel L5/40, eluents: successively hexane, CHCl<sub>3</sub> and acetone).

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