

## Stereospecific Access to Trisubstituted Enol Ethers from Vinylsilanes

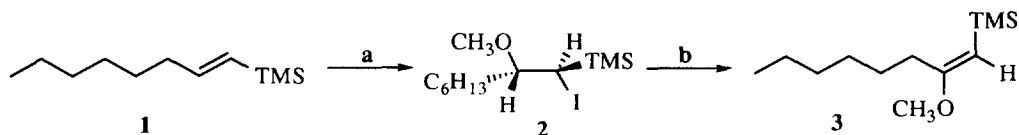
José Barluenga,<sup>\*</sup> Lorenzo J. Alvarez-García, Gustavo P. Romanelli and José M. González

Instituto Universitario de Química Organometálica "Enrique Moles"-Unidad Asociada al CSIC.  
Universidad de Oviedo. 33071 Oviedo, SPAIN

**Abstract:** The reaction of  $RCH=CHSiMe_3$  (R: alkyl or aryl) with  $IPy_2BF_4/HBF_4$  and a set of representative alcohols affords the corresponding addition products as a single regio- and stereoisomers in good yield. Subsequent dehydroiodination with DBU furnishes silyl-substituted enol ethers. © 1997 Elsevier Science Ltd.

Vinylsilanes are useful compounds in organic synthesis.<sup>1</sup> The well established ability of the silyl groups to hyperconjugatively stabilize an electron deficiency in the  $\beta$ -position (the so called  $\beta$ -effect)<sup>2</sup> usually accounts well for the selectivity in their reactions with electrophiles, mainly when carbon-silicon cleavage operates.<sup>3</sup> We reported that  $IPy_2BF_4$  is a convenient reagent to accomplish the iododesilylation of simple 1-trimethylsilyl-1-alkenes in a stereospecific manner.<sup>4</sup> Herein, we report the successful addition of alcohols and iodine to alkyl- and aryl-substituted vinylsilanes mediated by  $IPy_2BF_4$ . Furthermore, upon treatment with a hindered tertiary nitrogen base a stereospecific synthesis of  $\beta$ -silylenoethers is completed, otherwise compounds difficult to prepare in a simple way.<sup>5</sup>

Addition reactions of electrophilic iodine to vinylsilanes retaining the silyl group are known,<sup>6</sup> nevertheless, alcohols have been scarcely employed as nucleophiles.<sup>7</sup> Besides, the synthetic usefulness of these adducts have been restricted to its application for preparing simple iodoalkenes by fluoride or alkoxide induced elimination reaction. We have found that low temperature reaction of 1-trialkylsilyl-1-alkenes with  $IPy_2BF_4$  in a 1:1 mixture of  $CH_2Cl_2$  and  $CH_3OH$  furnishes the corresponding addition product in excellent yield after hydrolysis and conventional workup, as for instance depicted in Scheme 1 for the conversion of *trans*-1-TMS-1-octene (**1**, TMS: trimethylsilyl) in the adduct **2**.



a:  $IPy_2BF_4/2 HBF_4$ ,  $CH_3OH/CH_2Cl_2$ , from  $-60^\circ C$  to  $-40^\circ C$ , 3 h, 90% ; b: DBU,  $CH_2Cl_2$ , 16 h, 90%

Scheme 1

Two equivalents of  $HBF_4$  (54% ethereal solution) are added to neutralize pyridine, suppressing its competitive addition. Interestingly, desilylation was not an appreciable reaction under the reported conditions. Starting from the *cis*-isomer **4** a different addition product **5** was obtained in 76% yield, again as a single regio- and stereoisomer, see Table 1. The regiochemistry for these intermolecular processes<sup>8</sup> can be easily rationalized assuming control by the silyl groups, as in related electrophilic attacks to vinylsilanes.<sup>9</sup>

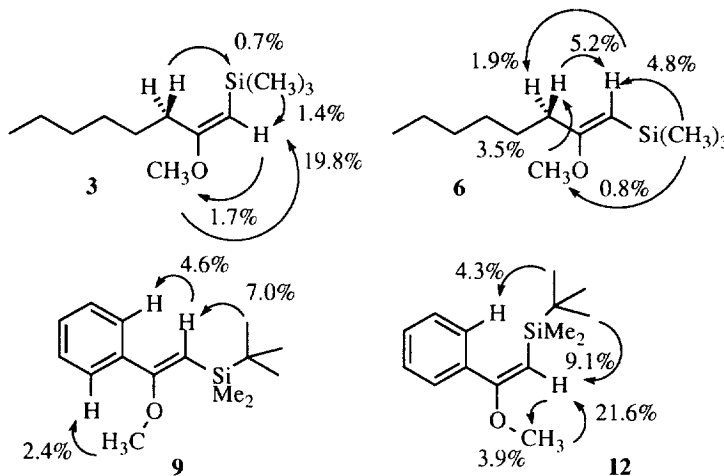
matching well recent findings in intramolecular addition of alcohols to vinylsilanes mediated by protic acids.<sup>10</sup>

TABLE 1 (See Scheme 1)

starting vinylsilane	nucleophile	adduct	enol ether
	MeOH		
	MeOH		
	MeOH		
	MeOH		
	<sup>i</sup> PrOH		
	<sup>i</sup> PrOH		
	<sup>i</sup> PrOH		
	<sup>i</sup> PrOH		
	<sup>t</sup> BuOH		
	<sup>t</sup> BuOH		
	<sup>t</sup> BuOH		
	<sup>t</sup> BuOH		

The reaction furnished a single diastereoisomer in each case. treatment of the adducts **2** and **5** with an excess of DBU (DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene) gave rise to their conversion to the enol ethers **3** and **6**,

respectively (see Scheme 1 Table1).<sup>11</sup> The overall transformation is synthetically of interest enabling the formal, clean and efficient replacement of H by a MeO group in the starting material. Furthermore, the later elimination step was helpful to trace the stereochemistry of the former addition of methanol. It is widely accepted that dehydroiodination of similar adducts takes place stereospecifically in an *anti* manner.<sup>7</sup> In keeping with this assumption, and considering the stereochemistry of the resulting enol ethers (see Scheme 2), it is reasonable to propose that reaction of alkylsubstituted terminal vinylsilanes with ROH and  $\text{IPy}_2\text{BF}_4$  gives rise to the addition products of **1** and RO arising from an *anti* approach, as depicted in Scheme 1 for the conversion of **1** to **2**.



Scheme 2. Representative NOE enhancements for enolethers **3**, **6**, **9** and **12**

The reaction of aryl-substituted TMS-vinylsilanes under the same conditions above described for **1** and **4** gave competition between addition and iododesilylation to a significant extent. Instead, this addition can be accomplished in a synthetically valuable form using the TBDMS-vinylsilanes **7** and **10** as starting compounds (TBDMS:  $\text{SiMe}_2\text{Bu}$ ). In this case, addition of alcohols takes place smoothly without noticeable loss of the silyl group (see Table 1). In this series, the reaction were run from  $-30\text{ }^\circ\text{C}$  to room temperature. For the addition of methanol the reaction was essentially completed in 5 h, whereas for the more hindered  $^i\text{PrOH}$  and  $^t\text{BuOH}$  took about 16 h (also, 16 h for the reaction of **1** and **2** with  $^i\text{PrOH}$  and  $^t\text{BuOH}$ , requiring longer reaction times than the incorporation of MeOH; for these nucleophiles, after mixing the reagents the reaction temperature was gradually rise from the initial  $-60\text{ }^\circ\text{C}$  up to rt). Interestingly, the addition of alcohols to the aryl substituted vinylsilanes **7** and **10** occurred following a *syn* addition mode,<sup>12</sup> as deduced from the stereochemistry of **9** and **12**, resulting after dehydroiodination with DBU of the corresponding adducts **8** and **11** (see Scheme 2)<sup>11</sup>. Contrary to the result from **1** and **4**, the enol ethers resulting from aryl-substituted vinylsilanes **7** and **10** were obtained with overall retention of the initial relationship between the silicon and the aryl chain. In short, an easy, versatile and stereospecific synthesis of silyl-containing trisubstituted enol ethers was developed starting from readily available vinylsilanes and relying in the efficiency of  $\text{IPy}_2\text{BF}_4$  to mediate a high-yielding, regio- and stereospecific addition of alcohols and iodine to the starting material.

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## References and Notes

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- All the compounds reported in Table 1 have been characterized by their <sup>1</sup>H and <sup>13</sup>C NMR, MS and IR spectra. Satisfactory elemental analyses were obtained for representative compounds. Besides, after elimination of HI by treatment with DBU and subsequent hydrolysis under acidic conditions, the herein described adducts yielded only ketones, further proving the proposed regiochemistry.
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