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Hydroselenation of alkynes using $NaBH_4/BMIMBF_4$: easy access to vinyl selenides

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Abstract—A general and easy method for the synthesis of several vinyl selenides using $NaBH_4$ and $BMIMBF_4$ as a recyclable solvent is described. This efficient and improved method furnishes the corresponding vinyl chalcogenides preferentially with *Z* configuration. We also observed that when the same protocol was applied to phenyl acetylene, (*E*)-bis-phenylseleno styrene was obtained in good yield and with high selectivity.

Vinyl selenides have been found to be a very useful tool in organic synthesis, since they are very versatile intermediates for the selective construction of isolated or conjugated olefins.[1] Besides, organoselenium compounds have attracted an increasing interest because of their useful biological activities.[2] On this way, various methods are mentioned for the preparation of vinyl selenides and the most common protocols involve the addition of organo selenols, or the respective chalcogenolate anions, to terminal or internal alkynes.[1b,3] On the other hand, ionic liquids (ILs) are receiving much attention in organic synthesis, both as recyclable solvents and/or catalysts.[4] Because product isolation or catalyst recycling is very easy in ILs and, in some cases, rate accelerations and/or selectivity improvements are also observed, they are regarded as environmentally friendly green solvents. In despite of the high versatility of vinyl selenides and the greener feature of ILs, the use of ionic liquids as solvent for hydroselenation reaction of alkynes was not described. As a continuation of our studies toward the development of new and cleaner methods for the synthesis of vinyl chalcogenides,[5] we report herein the results of the hydroselenation of alkynes using $NaBH_4/BMIMBF_4$ (Scheme 1).[6]

Initially, we chose propargyl alcohol (**1a**; 2 mmol) and diphenyl diselenide (**2**; 0.5 equiv) to establish the best conditions for the hydroselenation reaction. We examined the temperature, amount of IL, $NaBH_4$ and the use of N_2 atmosphere. It was found that using 0.046 g of $NaBH_4$ and 0.5 mL of IL at room temperature and under N_2 atmosphere, the reaction proceeded slowly and in 30% yield after stirring for 26 h. However, when the mixture was heated at 60 °C, the desired products **3a** and **4a** were obtained in good yield (87%) after 6 h (Table 1, entry 1). When the same protocol was performed without N_2, after 10 h, incomplete consumption of **2** was observed and the products were isolated in 48% yield. When the reaction was performed in the presence of $BMIMBF_4$ alone, without $NaBH_4$, no reaction took place in all conditions tested and the starting materials were recovered. Besides, using a smaller amount of $NaBH_4$ (0.038 g), the desired products **3a** and **4a** were obtained only in 52% yield.

Since the best conditions were established, the protocols were extended to other alkynyl alcohols (Scheme 1). In all the studied cases, a mixture of (*Z*)-**3** and *gem*-**4** was obtained in good yields (entries 1–5) and, except for homopropargyl alcohol (**1e**, entry 5), the anti-Markovnikov adduct **3** was obtained in higher amount than the Markovnikov one **4**. For the reaction of phenylselenolate anions with sterically hindered alcohols, it was observed that steric factors are important, because both, the **3**:**4** ratio and the reaction time, increase with the group R size (Table 1, compare entries 2–4 with 1 and 5). This regioselectivity is similar to that reported for the methods which use organic solvents.[1b,3] However, in a general way, using our IL based protocol,

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Keywords: Ionic liquids; Hydroselenation; Vinyl selenide.

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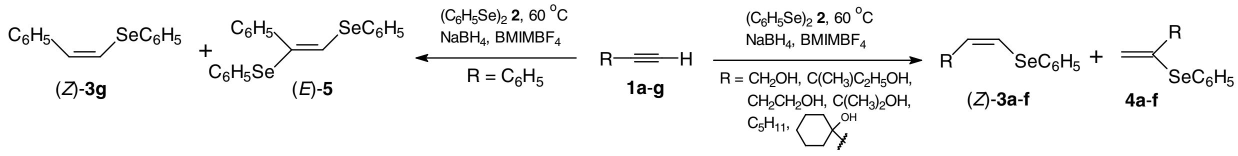
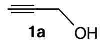
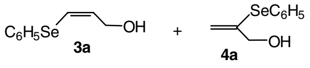
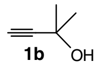
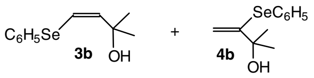
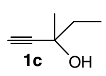
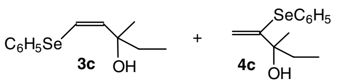
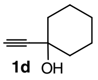
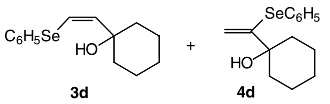
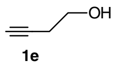
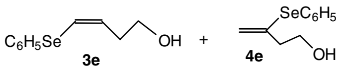
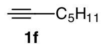
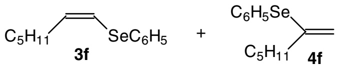
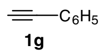
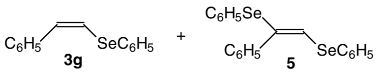


Scheme 1.

Table 1. Hydroselenation of Alkynes using $BMIMBF_4$ as recyclable solvent

Entry	Alkyne **1**	Products **3** + **4**	Time (h)	Yield[a] (%)	Ratio[b] (*Z*)-**3**:**4**
1			6	87	72:28
2			10	62	91:9
3			9	90	80:20
4			10	81	>95:5
5			6	74	44:56
6			9	Trace	—
7			3	85	[c]

[a] Yields of pure products isolated by column chromatography (hexanes/AcOEt) and identified by mass spectrometry, ^1H, ^{13}C NMR.

[b] Determined by GC of the crude reaction mixture and confirmed after isolation of the individual isomers.

[c] Obtained as mixture of (*Z*)-**3g** and (*E*)-**5** (**3g**:**5** ratio = 26:74).

the reaction time was reduced from days to hours, with gentle heating.[6] In addition, after completion of the reaction, the products are simply extracted with ether and the ionic liquid is reused without significant loss in yields. When the same protocol was applied to phenyl acetylene (**1g**), (*E*)-1,2-bis-phenylseleno styrene (**5**) was obtained in 63% yield after 3 h at 60 °C. This result is similar to that obtained under solvent-free conditions.[5a]

In conclusion, we have presented here a new methodology for the addition of selenolate anions to alkynyl alcohols and phenyl acetylene, under mild conditions and with non-aqueous work-up. This improved, simple, fast, and clean protocol uses recyclable ionic liquid as a solvent, as well as selectively affords mono- and bis-organoselenium alkenes.

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6. *General procedure for the synthesis of vinyl selenides*: To a mixture of propargyl alcohol (**1a**; 0.112 g; 2 mmol) and diphenyl diselenide (**2**; 0.157 g; 0.5 mmol) in BMIMBF$_4$ (0.5 mL) under N_2 atmosphere, NaBH$_4$ (0.046 g) was added at room temperature. Then, the temperature was slowly raised to 60 °C. The reaction progress was followed by TLC and after 6 h (see Table 1) the reaction mixture was extracted using ether (5 × 3 mL). The solvent was evaporated under reduced pressure and the residue was purified by column chromatography over silica gel eluting with hexanes/ethyl acetate (90:10), yielding products **3a** (0.136 g, 63%) and **4a** (0.052 g, 24%). (*Z*)-**3a**: ^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 7.43–7.54 (m, 2H); 7.22–7.27 (m, 3H); 6.58 (dt, $J = 9.4$ and 1.4 Hz, 1H); 6.19 (dt, $J = 9.4$ and 6.0 Hz, 1H); 4.24 (dd, $J = 6.0$ and 1.0 Hz, 2H); 3.02 (broad s, 1H); **4a**: 7.43–7.54 (m, 2H); 7.22–7.27 (m, 3H); 5.86 (s, 1H); 5.40 (s, 1H); 4.15 (s, 2H); 3.02 (broad s, 1H).[3a,e]