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SHORT COMMUNICATIONS

Synthesis of 2-(Vinylselanyl)pyridine

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Vinylselanyl derivatives are important intermediate products and building blocks in modern organic synthesis [1]. The main procedure for their preparation is based on nucleophilic addition of organylselenolate or selenide ions to acetylenes [1–3]. Organylselenolate ions can be generated *in situ* by reduction of organic diselenides [1, 2]. We have developed efficient methods for the preparation of divinyl selenide [4–6] and alkyl vinyl selenides [7, 8] via nucleophilic addition of selenolate and selenide ions.

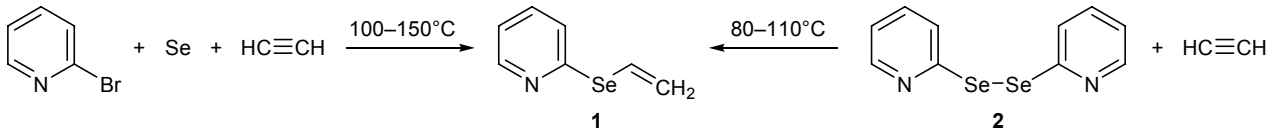
Prior to our studies, 2-(vinylselanyl)pyridine (**1**) was not reported in the literature. We have developed two procedure for the synthesis of this compound. One-pot reaction of elemental selenium with acetylene and 2-bromopyridine in a basic reducing system (BRS), KOH–DMSO (DMF, HMPA)–N_2H_4–H_2O, afforded 40–52% of **1** (Scheme 1). The best yield of **1** (52%) was obtained in HMPA.

Compound **1** is formed in four steps. The first step is generation of potassium diselenide from elemental selenium by the action of potassium hydroxide and hydrazine hydrate. In the second step, potassium diselenide reacts with 2-bromopyridine to give bis(pyridin-2-yl) diselenide (**2**). Diselenide **2** is then reduced to potassium pyridine-2-selenolate with hydrazine in the presence of KOH, and the final step is nucleophilic addition of pyridine-2-selenolate to acetylene (Scheme 2).

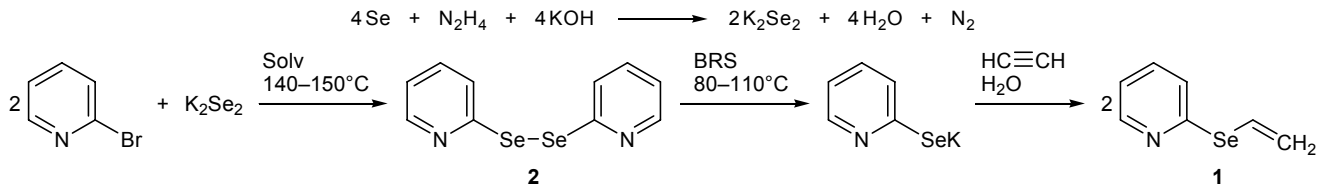
The second method is based on the reaction of acetylene with bis(pyridin-2-yl) diselenide (**2**) in the same basic reducing systems. This method ensures formation of **1** in 82–90% yield.

Selenium is an important trace element, and many organoselenium compounds exhibit high biological activity [9]. Many drugs contain a pyridine ring which may be regarded as a pharmacophoric group. Vinyl-

Scheme 1.



Scheme 2.



BRS stands for basic reducing system: KOH–Solv–N_2H_4–H_2O, Solv = DMSO, DMF, HMPA.

selanyl group can be subjected to functionalization, in particular it can be involved in electrophilic additions to a double bond [10]. Compound **1** is a promising intermediate product for organic synthesis, and its availability opens prospects in obtaining new biologically active alkylselanylpyridines.

2-(Vinylselanyl)pyridine (1). A mixture of 7.9 g (0.1 mol) of selenium, 9.2 g (0.14 mol) of 85% KOH, 12 mL of hydrazine hydrate, 17.4 g (0.11 mol) of 2-bromopyridine, and 100 mL of anhydrous HMPA was heated for 5 h at 140–150°C in a rotating high-pressure reactor. The mixture was left overnight, a solution of 20 g (3 mol) of 85% KOH in 20 mL of water and 20 mL of hydrazine hydrate were added, and the mixture was heated for 5 h at 100–110°C in a rotating high-pressure reactor while supplying acetylene to a pressure of 12 atm. The mixture was diluted with water and extracted with ethyl acetate, the organic phase was washed with water and dried over Na_2SO_4, and the solvent was distilled off. The residue was purified by column chromatography (silica gel; chloroform–hexane, 3:1). Yield 9.57 g (52%), light yellow oily liquid with a characteristic odor. ^{1}H NMR spectrum, δ, ppm: 5.86 d (1H, $=CH_2$, ^3J = 10 Hz), 5.70 d (1H, $=CH_2$, ^3J = 17 Hz), 7.01 m (1H, SeCH=), 7.45–7.24 m (3H, C_5H_4N), 8.42 m (1H, C_5H_4N). ^{13}C NMR spectrum, δ_C, ppm: 118.94 ($=CH_2$), 119.77 (C_5H_4N), 123.68 (SeCH=), 124.18 (C_5H_4N), 125.96 (C_5H_4N), 135.22 (C_5H_4N), 149.56 (C_5H_4N). Found, %: C 45.97; H 4.01; N 7.42; Se 43.12. C_7H_7NSe. Calculated, %: C 45.67; H 3.83; N 7.61; Se 42.89.

The NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker DPX-400 spectrometer at 400.13 and 100.61 MHz, respectively, using hexamethyldisiloxane as reference.

The spectral data were obtained using the equipment of the Baikal Joint Analytical Center (Siberian Branch, Russian Academy of Sciences). This study was performed under financial support by the Russian Foundation for Basic Research (project no. 14-03-92705_Ind).

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