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A novel method for the synthesis of 2,5-diarylselenophenes

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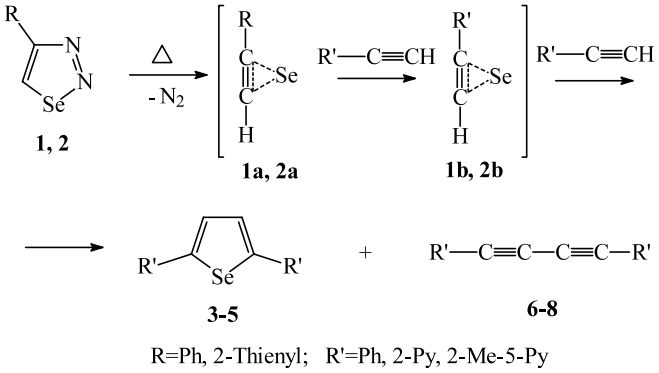
Abstract—The reaction of 4-phenyl- or (2-thienyl)-1,2,3-selenadiazoles with 10 equiv. of arylacetylenes leads to the formation of 2,5-diarylselenophenes in moderate to good yields and 1,4-diarylbuta-1,3-diynes as by-products.

Recently, the syntheses of selenium containing compounds and the further utilization of these compounds in organic synthesis has steadily increased.[1] The interest in 1,2,3-selenadiazoles stems from the fact that they undergo a wide variety of reactions as 1,3-dipoles or as a source of selenium and hence have attracted much attention for the synthesis of different organoselenium compounds. The cleavage of 5-unsubstituted 1,2,3-selenadiazoles with the loss of a nitrogen molecule and formation of alkynylselenolates was observed under the action of strong bases (BuLi, EtOK, etc.).[2a–c] Pyrolysis of 1,2,3-selenadiazoles leads to the elimination of N_2 and elemental selenium to give acetylenes in good yields.[2d–f] Prolonged heating of 4-arylselenadiazoles affords 2,5-diarylselenophenes in high yields. In the case of 4-phenyl-1,2,3-selenadiazole the reaction carried out at 140°C yields only 2,5-diphenylselenophene, at higher temperatures (240–250°C) 2,5-diphenylselenophene was isolated as the major product along with small quantities of isomeric 2,4-diphenylselenophene.[3] It has been shown that 1,2,3-selenadiazoles may serve as the precursors for the synthesis of cobalt, palladium, and platinum complexes, containing various selenium ligands.[4] The reaction of selenadiazoles derived from cyclic ketones with an excess of olefins or dienes (hept-1-ene, methyl acrylate, methyl methacrylate, acrylonitrile, methyl vinyl ketone, 2-methylbuta-1,3-diene, 2,3-dimethylbuta-1,3-diene, and hexa-1,5-diene) in the presence of a catalytic amount of tributylstannane or allyltributylstannane and AIBN proceeds with the formation of dihydroselenophenes (16–76%). In contrast, when 1,2,3-selenadiazoles prepared from linear and aromatic ketones were used as substrates, the radical-catalyzed reaction did not take place, and alkynes were formed as the sole products.[5]

In the current report we investigate the interaction of intermediates obtained by thermolysis of 4-phenyl- (**1**) and 4-(2-thienyl)selenadiazoles (**2**)[6] with arylacetylenes leading to formation of disubstituted selenophenes. Thermal decomposition of selenadiazoles **1** and **2** in the presence of 2 equiv. of arylacetylene proceeds without selectivity giving a mixture of three different symmetrical and unsymmetrical selenophenes in low yields. To increase the selectivity of this reaction we optimized the arylacetylene:selenadiazole ratio. It was found that only one 2,5-diarylselenophene (**3**–**5**) was obtained using a 10-fold excess of arylacetylene. In all cases the reaction was accompanied by the formation of 1,4-diarylbuta-1,3-diynes **6**–**8**[7] (Scheme 1). The mechanism of this reaction includes the thermal elimination of nitrogen and the formation of intermediates **1a** and **2a**. During the second step the intermediates **1a** and **2a** are converted into species **1b** and **2b** by reaction with the arylacetylene (R′–C≡CH). Subsequently, intermediates



Scheme 1.

Keywords: selenadiazole; selenophene; butadiyne.

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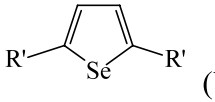
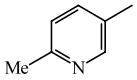
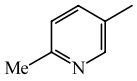
Table 1. 2,5-Diarylselenophenes from thermal decomposition of selenadiazoles **1** and **2** in the presence of arylacetylenes

Entry	R	R'	 (Yield, %)
1	Ph		**3** (52) [3]
1	Ph		**4** (80) [8]
2		Ph	**5** (20) [6]
2			**3** (15) [3]
2			**4** (42) [8]

1b and **2b** react with a second molecule of the arylacetylene to yield the corresponding 2,5-diarylselenophenes (**3**–**5**) and 1,4-diarylbutadi-1,3-ynes (**6**–**8**). The yields of selenophenes **3**–**5** are presented in Table 1. As can been seen from the results presented, the application of 4-phenyl-1,2,3-selenadiazole **1** for the synthesis of 2,5-diarylselenophenes is preferable to the use of the thienyl analogue **2**. In this case 4-phenylselenadiazole **1** serves as the source of selenium for the formation of 2,5-diphenylselenophenes **3**–**5** in contrast to the tributylstannyl radical-catalyzed decomposition of 4-phenylselenadiazole in the presence of olefins giving phenylacetylene.[5]

Our attempts to prepare 2,5-bis(trimethylsilyl)- and 2,5-bis(*tert*-butyl)selenophenes from **1** and **2** with an excess of trimethylsilylacetylene and 3,3-dimethylbut-1-yne failed. Only 2,5-diphenyl- or 2,5-di(2-thienyl)selenophenes were obtained as products of selenadiazole decomposition.

In summary, we have developed a simple method for the preparation of 2,5-diarylselenophenes from 4-phenyl- and 4-(2-thienyl)-1,2,3-selenadiazoles.

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8. A mixture of 4-phenyl-1,2,3-selenadiazole **1** (0.104 g, 0.5 mmol) and 2-methyl-5-ethynylpyridine (0.59 g, 5 mmol) in benzene (2 ml) was refluxed for 3 h. The pure product **4** was isolated by column chromatography on silica gel with ethyl acetate as eluent. Mp 91–93°C; 80% yield; MS, *m*/*e* 314 [$M^{\bullet+}$, 100], 299 [$M^{\bullet+}$–15, 10], 233 [$M^{\bullet+}$–Se, 18]; ^{1}H NMR (200 MHz, $CDCl_3$/TMS) δ (ppm): 2.55 (6H, s, Me), 7.12 (2H, d, $J=8.3$ Hz), 7.43 (2H, s, CH), 7.55 (2H, dd, $J=8.2$ Hz, $J=2.2$ Hz), 8.68 (2H, d, $J=2.2$ Hz); ^{13}C NMR (50.31 MHz, $CDCl_3$/TMS) δ (ppm): 24.1, 115.9, 123.3, 125.9, 137.5, 146.2, 152.4, 157.7; anal. calcd for $C_{16}H_{14}N_2Se$: C, 61.33; H, 4.51; N, 8.94. Found: C, 61.21; H, 4.59; N, 9.03%.