3-Vinyl-1,2,5-selenadiazole

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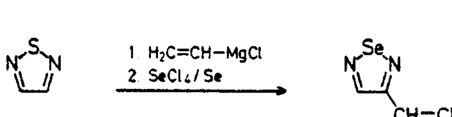
The potential applicability of 3-vinyl-1,2,5-selenadiazole (**2**) for the synthesis of polyfunctional polymers containing *vic*-diamino, *vic*-diimino, or *vic*-dicarbonyl groups led us to search for a convenient synthesis of this heterocyclic compound which we first obtained by a rather laborious conventional method. As a result, we now present a one-pot procedure (Method A) for the synthesis of **2** starting from 1,2,5-thiadiazole (**1**). The method consists of the reaction of **1** with vinylmagnesium chloride in ether/tetrahydrofuran followed by treatment with selenium(I) chloride [generated from selenium(IV) chloride and selenium].



1 **2**

The yield of **2** is only 10%; nevertheless, the method is practically useful because it is easy to perform and the reagents are readily accessible. The method may also be applied to the synthesis of other 1,2,5-selenadiazoles by using other Grignard reagents, the yields being moderate in some cases.

The reaction which, in summary, represents the *C*-vinylation of **1** accompanied by S/Se exchange might proceed via initial nucleophilic attack at the S-atom and subsequent cleavage of the 1,2,5-thiadiazole ring, as previously postulated for disubstituted thiadiazole derivatives[1].

Our above-mentioned first synthesis of 3-vinyl-1,2,5-selenadiazole (**2**) (Method B) consists of the allylic tosylamination of 4-tosylamino-1-butene (**3**) with ditosylsulfurdiimide (**4**) in dichloromethane, detosylation of the resultant 3,4-bis[tosylamino]-1-butene (**5**) using naphthalene-sodium[7]

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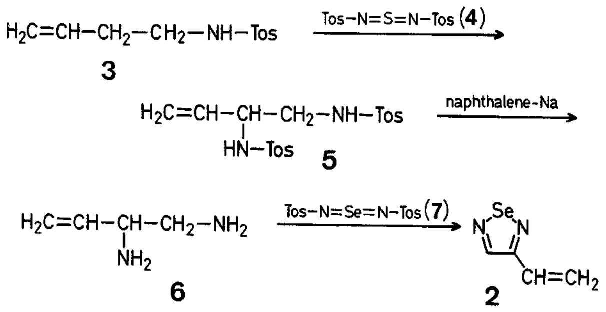
addition compound in dimethoxyethane, and cyclocondensation of the 3,4-diamino-1-butene (**6**) obtained upon hydrolysis with ditosylseleniumdiimide (**7**) in dichloromethane.



The tosylamination of **3** in the allylic position using ditosylsulfurdiimide (**4**) represents an extension of the method of Sharpless and Hori[2] to a substrate which already contains a tosylamino group on the neighboring C-atom.

Ditosylseleniumdiimide (**7**) has hitherto not been used in cyclocondensation reactions of the above type. This reagent was chosen because other Se synthons such as selenium dioxide or chloride[3] could not be used in the cyclocondensation with 3,4-diamino-1-butene (**6**); their use led only to the formation of tars.

Several metal salts, e.g., cadmium chloride, form stable complexes with compound **2**.

Compound **2** readily polymerizes and copolymerizes in the presence of radical initiators to afford macromolecules containing unaltered 1,2,5-selenadiazole rings.

The structure of compound **2** is in accord with microanalysis, mass spectrum, I.R.-, and ^{1}H-N.M.R. spectra.

3-Vinyl-1,2,5-selenadiazole (2):

Method A: Anhydrous ether (260 ml) is added to a solution (76 ml, 0.18 mol) of vinylmagnesium chloride in tetrahydrofuran under nitrogen. The solution is cooled to $-60°$ and a solution of 1,2,5-thiadiazole (**1**; 5.07 g, 58.87 mmol) in anhydrous ether (60 ml) is added dropwise with stirring over ~30 min. The mixture is stirred at $-60°$ for a further hour. Then, selenium(I) chloride [prepared immediately before use by heating to homogenization selenium(IV) chloride (22.08 g, 0.10 mol) and elemental selenium (23.69 g, 0.30 mol)] is added dropwise to the stirred mixture. After the addition is complete, the cooling bath is removed and stirring is continued for 1 h. The mixture is then poured into ice water (200 ml), acidified with a few drops of hydrochloric acid, and subjected to rapid steam distillation. The distillate is saturated with ammonium sulfate, extracted with peroxide-free ether, and the extract dried with sodium sulfate. The solvent is removed and the residue distilled in vacuo; yield: 0.983 g (10%); b.p. 78°/0.4 torr. The product may be further purified by crystallization from pentane/ether at low temperature.

$C_4H_4N_2Se$	calc.	C 30.21	H 2.54	N 17.61
(159.0)	found	30.48	2.56	17.52

M.S.: $m/e = 160$ (M$^+$, 69), 133 (100), 107 (42), 80 (71).

I.R. (film): $\nu = 1610$, 985, 925 (vinyl group); 718, 435 cm^{-1} (ring).

^{1}H-N.M.R. (CCl_4): $\delta = 9.8$ (s, 1H, ring); 7.4 (q, 1H, vinyl CH); 6.7–6.1 ppm (dq, 2H, vinyl CH_2).

Similarly obtained:

3-phenyl-1,2,5-selenadiazole; yield: 46%; m.p. 85–85.5°.

$C_8H_6N_2Se$	calc.	45.95	2.89	13.40
(209.1)	found	45.98	2.91	13.36

M.S.: $m/e = 210$ (M$^+$, 85), 183 (57), 107 (8), 103 (100), 80 (9).

Method B:

3,4-Bis[tosylamino]-1-butene (**5**): A mixture of 4-tosylamino-1-butene[5] (**3**; 5.585 g, 24.79 mmol), dichloromethane (140 ml), and ditosylsulfurdiimide[6] (**4**; 10.121 g, 27.32 mmol) is allowed to stand at room temperature for 30 h. The solvent is then removed and the residue stirred with a solution of potassium carbonate (22 g) in water (80 ml) + methanol (120 ml) for 20 h at room temperature. The mixture is extracted with ether (1 × 200 ml), the extract dried with sodium sulfate, and the volatile products (ether, methanol) are removed in vacuo. The residue is washed with boiling ether (1 × 20 ml) and with boiling water (3 × 30 ml) and the residual product is crystallized from benzene; yield: 4.889 g (50%); m.p. 137–139°.

$C_{18}H_{22}N_2O_4S_2$	calc.	C 54.80	H 5.62	N 7.10	S 16.26
(394.5)	found	55.10	5.62	7.17	16.55

3,4-Diamino-1-butene (**6**): Sodium (3.244 g, 0.141 mol) is added in small portions to a stirred solution of naphthalene (19.80 g, 0.154 mol) in anhydrous dimethoxyethane (240 ml) at room temperature. Stirring is continued for 2 h and then a solution of 3,4-bis[tosylamino]-1-butene (**5**; 6.956 g, 17.63 mmol) in dimethoxyethane (65 ml) is added. The mixture is stirred for a further hour, and then diluted with ether (200 ml). Ice (1 g) is added and the mixture is extracted with 1 normal hydrochloric acid (3 × 15 ml). The acid extract is evaporated in vacuo, ether (50 ml) is added to the residue, the mixture is cooled in ice, saturated aqueous potassium hydroxide (~5 ml) is added, and the mixture extracted with ether (10 × 15 ml). The extract is dried with potassium hydroxide pellets, the solvent removed, and the residual product distilled in vacuo; yield: 0.472 g (31%); b.p. 57–60°/20 torr.

$C_{18}H_{18}N_2O_2$	calc.	C 73.45	H 6.16	N 9.52
(294.4)	found	73.71	6.20	9.39

I.R. (film): $\nu = 3320$, 3240 (amino group); 3035; 1610, 985, 915 cm^{-1} (vinyl group).

Dibenzoyl Derivative: m.p. 178–180°.

3-Vinyl-1,2,5-selenadiazole (**2**): To a stirred suspension of ditosylseleniumdiimide[4] [**7**; generated *in situ* from selenium (2.507 g, 31.75 mmol) and anhydrous chloramine-T (12.521 g, 55.00 mmol)] in dry dichloromethane (150 ml) is added dropwise a solution of 3,4-diamino-1-butene (**6**; 1.129 g, 13.11 mmol) in dichloromethane (30 ml). Stirring is continued for 1 h at room temperature. The mixture is hydrolyzed by adding a solution (80 ml) prepared from sodium sulfite (3 g), sodium hydroxide (20 g), and water (250 ml). The mixture is filtered and extracted with dichloromethane (3 × 70 ml). The extract is dried with sodium sulfate and the solvent is removed on a rotary evaporator. The residue is extracted with boiling pentane (3 × 50 ml), the solvent is removed from the extract, and the residual product is distilled in vacuo; yield: 0.396 g (19%); b.p. 78°/0.4 torr.

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