A Facile Synthesis of 3,5-Diaryl- and 3,5-Diheteroaryl-1,2,4-selenadiazoles

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The two first 1,2,4-selenadiazoles were synthesized[1] in 1904 by treatment of selenocarboxamides with iodine; yields and physical data of the products were not given. More recently,

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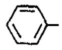
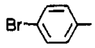
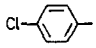
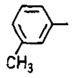
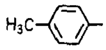
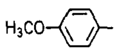
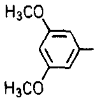
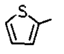
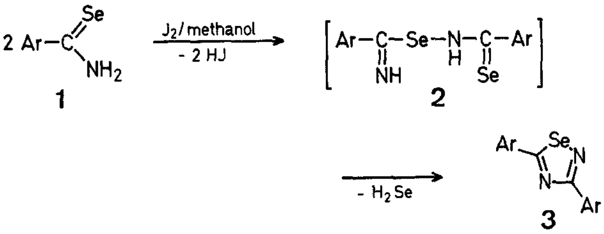
Table 1. 3,5-Disubstituted 1,2,4-Selenadiazoles (**3**)

3	Ar	Yield [%]	m.p. (from solvent)	Molecular formula[a]
a		42	85° (ethanol)	$C_{14}H_{10}N_2Se$ (284.2)
b		52	162° (propanol)	$C_{14}H_8Br_2N_2Se$ (443.0)
c		86	168° (butanol)	$C_{14}H_8Cl_2N_2Se$ (354.1)
d		40	69° (methanol)	$C_{16}H_{14}N_2Se$ (313.3)
e		48	122°[b] (ethanol)	$C_{16}H_{14}N_2Se$ (313.3)
f		37	139° (ethanol)	$C_{16}H_{14}N_2O_2Se$ (345.3)
g		74	132° (ethanol)	$C_{18}H_{18}N_2O_4Se$ (405.3)
h		35	98° (ethanol)	$C_{10}H_6N_2S_2Se$ (296.3)

[a] The microanalyses of all products were in good accord with the calculated values: C, ±0.20; H, ±0.12; N, ±0.14; Se, ±0.25.

[b] Ref. [1], m.p. 116°.

5-amino-3-alkyl- and 5-amino-3-aryl-1,2,4-selenadiazoles were prepared from *N*-haloamidines and potassium selenocyanate[2]. Based on the brief report of Ref. [1] we have now worked out a facile general synthesis of 3,5-diaryl-1,2,4-selenadiazoles (**3**) and its 3,5-bis[2-thienyl] analog from the readily available areneselenocarboxamides[3] (**1**) (thiophene-2-selenocarboxamide, respectively) and iodine in methanol. The reaction is assumed to proceed by oxidative *N—Se* coupling of **1** and subsequent ring closure of the open-chain intermediate **2** with elimination of hydrogen selenide.



Compounds **3** are thus obtained in yields of 35–86%. The structures of compounds **3** were established on the basis of microanalyses, mass-spectral fragmentation, and ^{1}H-N.M.R. data.

The mass spectra were recorded using a Varian-Mat CH7A instrument. The ^{1}H-N.M.R. spectra were recorded on a Varian EM-360

Table 2. Mass Spectra and ^{1}H-N.M.R. Data of Compounds **3**

3	Mass Numbers (calculated on the basis of ^{78}Se and ^{80}Se)	M.S. *m/e*	^{1}H-N.M.R. Solvent	^{1}H-N.M.R. δ [ppm]
a	284; 286	51 (9); 76 (23); 77 (14); 103 (70) $C_6H_5-C\equiv\overset{+}{N}$; 181 (50); 183 (100) $C_6H_5-N=C=\overset{+}{Se}$; 284 (8); 286 (16)	DMSO-d_6	7.60 (6H, m); 8.25 (4H, m)
b	442; 444	51 (12); 75 (20); 102 (66); 180 (20); 181 (36) 4-$BrC_6H_4-C\equiv\overset{+}{N}$; 182 (47); 183 (35); 259 (48); 261 (100) 4-Br$-C_6H_4-N=C=\overset{+}{Se}$; 263 (78); 442 (13); 444 (16)	DMSO-d_6	7.60–7.88 (4H); 7.89–8.32 (4H)
c	352; 354; 356	51 (7); 75 (13); 102 (31); 137 (80) 4-Cl$-C_6H_4-C\equiv\overset{+}{N}$; 139 (27); 215 (48); 217 (100) 4-Cl$-C_6H_4-N=C=\overset{+}{Se}$; 219 (43); 352 (6); 354 (13); 356 (8)	pyridine-d_5	7.88–8.15 (4H); 8.32–8.60 (4H)
d	312; 314	89 (22); 90 (24); 115 (64); 117 (77) 3-$H_3C-C_6H_4-C\equiv\overset{+}{N}$; 195 (60); 197 (100) 3-$H_3C-C_6H_4-N=C=\overset{+}{Se}$; 312 (11); 314 (22)	DMSO-d_6	2.42 (6H, s); 7.22–7.65 (4H); 7.78–8.25 (4H)
e	312; 314	89 (17); 90 (24); 116 (52); 117 (71) 4-$H_3C-C_6H_4-C\equiv\overset{+}{N}$; 195 (51); 197 (100) 4-$H_3C-C_6H_4-N=C=\overset{+}{Se}$; 312 (9); 314 (18)	DMSO-d_6	2.40 (6H, s); 7.20–7.50 (4H); 7.87–8.30 (4H)
f	344; 346	90 (14); 103 (13); 133 (100) 4-$H_3CO-C_6H_4-C\equiv\overset{+}{N}$; 211 (24); 213 (48) 4-$H_3CO-C_6H_4-N=C=\overset{+}{Se}$; 344 (7); 346 (14)	DMSO-d_6	3.85 (6H, s); 6.90–7.23 (4H); 7.90–8.37 (4H)
g	404; 406	65 (4); 77 (4); 90 (3); 103 (14); 120 (4); 133 (10); 134 (9); 149 (4); 163 (100) 3.5-$(H_3CO)_2C_6H_3-C\equiv\overset{+}{N}$; 203 (4); 241 (22); 243 (45) 3,5-$(H_3CO_2C_6H_3-N=C=\overset{+}{Se}$; 404 (8); 406 (17)	DMSO-d_6	3.85 (12H, s); 6.50–6.87 (2H, m); 7.10–7.50 (4H)
h	296, 298	39 (12); 45 (24); 58 (18); 109 (100) $C_4H_3S-C\equiv\overset{+}{N}$; 187 (45); 189 (91) $C_4H_3S-N=C=\overset{+}{Se}$; 296 (14); 298 (30)	DMSO-d_6	7.22 (2H, m); 7.85 (2H, m); 8.15 (2H)

N.M.R. spectrometer using TMS as internal standard. The melting points were determined on a Kofler hot-bench apparatus. The microanalyses were performed by Dornis & Kolbe, Mikroanalytisches Laboratorium, Hohenweg 17, D-4330 Mülheim/Ruhr, West Germany.

3,5-Diaryl- and 3,5-Bis[2-thienyl]-1,2,4-selenadiazoles (3):
The selenocarboxamide **1** (0.01 mol) is added to a hot solution of iodine (2.8 g, 0.011 mol) in methanol (30 ml). The mixture is refluxed for 1 min, then cooled, and poured into cold water (150 ml). The solid which separates is isolated by filtration, dried, and recrystallized from the solvent given in Table 1.

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[1] W. Becker, J. Meyer, *Ber. Dtsch. Chem. Ges.* **37**, 2550 (1904).

[2] J. Goerdeler, D. Gross, H. Klinke, *Chem. Ber.* **96**, 1289 (1963).

[3] V. I. Cohen, *Synthesis* **1978**, 668.

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