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CYCLIC ARYLENEAZACHALCOGENENES

PART III [1] SYNTHESIS OF POLYFLUORINATED 2,1,3-BENZOTHIA-(SELENA)DIAZOLES

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SUMMARY

1-(4-X-Tetrafluorophenyl)-3-trimethylsilyl-1,3-diaza-2-thiaallenes (X = H, CH_3, Br, F, CF_3) treated with CsF in acetonitrile or THF cyclized to 6-X-4,5,7-trifluoro-2,1,3-benzothiadiazoles whose reduction led to the corresponding 1,2-diaminobenzenes. Cyclization of the latter with $SeCl_4$ gave 6-X-4,5,7-trifluoro-2,1,3-benzoselenadiazoles.

RESULTS AND DISCUSSION

Polyfluorinated 2,1,3-benzothia(selena)diazoles have been unknown earlier, except for the 4,5,6,7-tetrafluoro-derivative synthesized by cyclization of 1,2-diamino-3,4,5,6-tetrafluorobenzene with the tetrahalide of the respective chalcogen [2]. We have found that a convenient general method for the synthesis of 6-X-4,5,7-trifluoro-2,1,3-benzothiadiazoles (**1**) in 50 to 85 % yields is the intramolecular nucleophilic cyclization [3] of 1-(4-X-tetrafluorophenyl)-3-trimethylsilyl-1,3-diaza-2-thiaallenes (**2**) [4] under the action of CsF in acetonitrile (X = H, CH_3, Br, F) or THF (X = CF_3). This is the new example of synthesis of 2,1,3-benzothiadiazoles without the use of 1,2-diaminobenzenes. The reaction of arylamines with $(NSCl)_3$ including the vicarious nucleophilic substitution of hydrogen was used for this purpose previously [5].

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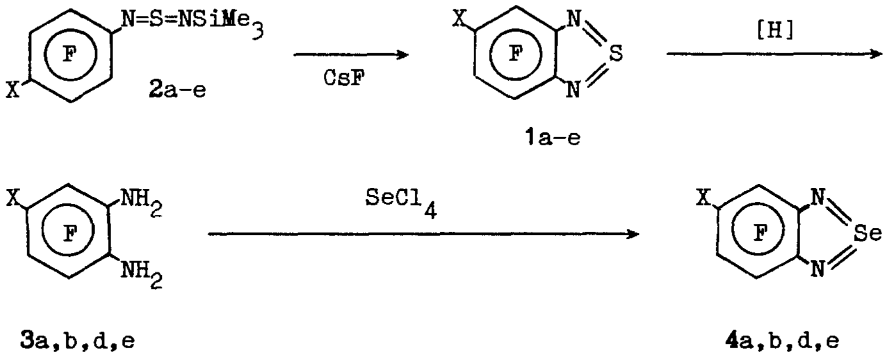
The reduction of compounds **I** with $SnCl_2$ or $NaBH_4$ ($X = CF_3$) afforded corresponding polyfluorinated 1,2-diaminobenzenes (**3**) in 75 to 85 % yields. The reactions of compounds **3** with $SeCl_4$ in monoglyme in the presence of pyridine led to 6-X-4,5,7-trifluoro-2,1,3-benzoselenadiazoles (**4**) in 85 to 90 % yields.



X = H (a), CH_3 (b), Br (c), F (d), CF_3 (e)

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were recorded on a Varian A56/60A spectrometer (60 and 56.4 MHz respectively, internal standards HMDS and C_6F_6); the mass-spectra (EI, 70 eV), on a Finnigan MAT MS-8200 spectrometer; the UV-visible spectra, on a Specord UV-Vis instrument.

Caesium fluoride was calcinated immediately before use. Compounds **1a,b,d** were reduced with $SnCl_2$/HCl to compounds **3a,b,d** under the conditions described in [6]. The compounds **1d**, **3a,d** and **4d** were known previously [2,7,8]. The syntheses given below, except for that of compound **3e**, were carried out under argon in absolute solvents. The data for compounds synthesized are listed in Tables 1 and 2.

TABLE 1

The Compounds Synthesized

Compound	Yield, %	M.p., °C [a] B.p., °C/mm	Formula	M^+, m/z [b] measured	calculated
1a	63	37-38	$C_6HF_3N_2S$	189.9799	189.9812
1b	87	40-41	$C_7H_3F_3N_2S$	203.9962	203.9969
1c	66	27-28.5	$C_6BrF_3N_2S$	267.8904	267.8918
1d	60	55-56 [c]	$C_6F_4N_2S$		
1e	52	94-95/13	$C_7F_6N_2S$	257.9682	257.9686
3a	82	75-76 [d]	$C_6H_5F_3N_2$	162.0391	162.0405
3b	81	98-99	$C_7H_7F_3N_2$	176.0559	176.0561
3d	85	130-131 [e]	$C_6H_4F_4N_2$		
3e	75	33.5-34.5	$C_7H_4F_6N_2$	230.0267	230.0278
4a	88	169-170	$C_6HF_3N_2Se$	237.9238	237.9257
4b	85	161-162	$C_7H_3F_3N_2Se$	251.9399	251.9413
4d	91	202-203 [f]	$C_6F_4N_2Se$		
4e	85	144-145	$C_7F_6N_2Se$	305.9130	305.9138

[a] Compounds **4**, in a sealed capillary

[b] For compound **1c**, ^{79}Br; for compounds **4**, ^{80}Se

[c] 51-52° [2]

[d] 74.6-75.2° [7]

[e] 131-131.5° [8]

[f] 202-203° [2]

6-X-4,5,7-Trifluoro-2,1,3-benzothiadiazoles (1a-e)

To a stirred suspension of 1.52 g (0.01 mol) of CsF in 200 ml of acetonitrile was added dropwise during 2 h, with boiling, a solution of 0.01 mol of compound **2a-d** in 30 ml of acetonitrile (in the case of **2e**, the same amount of THF was used). The mixture was boiled for 0.5 h, cooled to 20°C, filtered and solvent was distilled off at reduced pressure. The residue was chromatographed on an Al_2O_3 column (hexane-ether 3:1) and sublimed or distilled in vacuum. Compounds **1a-d** are colourless crystals; **1e**, a colourless liquid.

TABLE 2

NMR and UV Spectral Data

Com-pound	NMR chemical shifts, δ , ppm [a]		UV, λ_{max}, nm, (lg ε) [b]
	^{1}H	^{19}F	
1a	7.30	41.7, 27.6, 11.4	333(3.44, sh), 307(4.06), 302(4.03), 296(4.02)
1b	2.39	35.9, 24.5, 10.0	343(3.33, sh), 314(4.05), 308(4.01), 302(4.01)
1c		48.6, 33.6, 14.5	316(4.04), 308(4.01)
1d		14.3, 9.3	326(3.39, sh), 308(3.99), 302(3.97), 296(3.94)
1e		105.5, 44.9, 22.9, 14.2	329(3.45), 305(3.92), 300(3.90), 294(3.88)
3a	6.33, 3.41	24.9, 14.4, -1.8	283(3.32), 238(4.00)
3b	3.33, 2.06	19.7, 9.1, -2.1	285(3.27), 233(4.05)
3e	4.03, 3.22	107.4, 23.3, 14.2, -1.5	292(3.68), 254(4.10)
4a	7.66	42.1, 24.3, 10.7	328(4.24), 243(3.87)
4b	2.30	36.5, 21.6, 10.9	334(4.18), 234(3.76, sh)
4d		13.7, 6.7	327(4.13), 237(3.65)
4e		107.1, 46.6, 18.3, 13.6	330(4.07), 248(3.87)

[a] Solvents: 1a,b,c,e, **3a,b,e**, $CDCl_3$; 1d, CCl_4; **4a**, DMSO-d_6;
4b,d,e, dioxane.

[b] In ethanol, 1d in heptane.

5-Trifluoromethyl-3,4,6-trifluoro-1,2-diaminobenzene (**3e**)

To a stirred solution of 0.01 mol of compound 1e in 30 ml of ethanol was added portionwise, at 20°C, 0.02 mol of $NaBH_4$. After 1 h the solution was acidified with HCl, filtered, neutralized with aqueous Na_2CO_3 and extracted with ether. The extract was dried over $CaCl_2$, the solvent distilled off at reduced pressure and residue sublimed in vacuum. Compound **3e** is colourless crystals.

6-X-4,5,7-Trifluoro-2,1,3-benzoselenadiazoles (**4**a,b,d,e)

To a stirred solution of 0.003 mol of compound **3**a,b,d,e and 0.95 g (0.012 mol) of pyridine in 15 ml of monoglyme was added dropwise at 0^oC a solution of 0.66 g (0.003 mol) of $SeCl_4$ in 5 ml of monoglyme. The mixture was stirred for 1 h at 20^oC, the solution was filtered, the solvent distilled off at reduced pressure, the residue recrystallized from ethanol and sublimed in vacuum. Compounds **4** are yellow crystals.

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