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Substituted 1,3,2,4-Benzodithiadiazines and Related Compounds*

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ABSTRACT: *Despite some limitations, the 1:1 condensation of n-RC_6H_4-N=S=N-$SiMe_3$ (n = 2, 3, 4; R = CH_3, OCH_3, F, Cl, CF_3) with SCl_2, followed by intramolecular electrophilic ortho-cyclization, was found to be a general synthetic approach to the corresponding 5-R, 6-R, and 7-R–substituted 1,3,2,4-benzodithiadiazines, formally antiaromatic 12π-electron compounds. For precursors with n = 3, the high regioselectivity of the cyclization resulted in exclusive (R = OCH_3, F) or predominant (R = CH_3, Cl) formation of 6-R isomers; the ratio of the major 6-R isomer to the minor 8-R one was found to be 72:28 (R = CH_3) or 78:22 (R = Cl). The preferred direction of cyclization is consistent with thermodynamics of the corresponding intermediate σ-complexes as well as factors of kinetic control for an orbital-controlled El-Nu reaction. According to the X-ray diffraction data, the molecules of 5-CF_3 (**15**) and 6-F (**12**) derivatives are nearly planar, while the molecules of 5-OCH_3 (**7**) and 6-CH_3 (**4**) derivatives are bent along the $S^1 \ldots N^4$ line by ~11° (**7**) or 7° (**4**). An attempt to adopt CsF-induced intramolecular nucleophilic ortho-cyclization of Ar_F-S-N=S=N-$SiMe_3$ into polyfluorinated 1,3,2,4-benzodithiadiazines for polyfluoropyridine derivatives resulted in formation of polyfluorinated aminopyridines. Data obtained are consistent with a previously suggested scheme of sulfur–nitrogen chain shortening during cyclization. Mild acid hydrolysis of the title compounds was shown to be a convenient synthetic route to substituted 2,2′-diaminodiphenyl disulfides (including polyfluorinated ones) via the corresponding 2-aminobenzenethiols.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 113–124, 1999

INTRODUCTION

Recently, the synthesis of 1,3,2,4-benzodithiadiazine (**1**) [3] and its 5,6,7,8-tetrafluoro derivative (**2**) [4] was described. These are 12π-electron, formally antiaromatic [5], but thermodynamically quite stable compounds [6–8]. Their chemistry has been investigated only to a slight degree [3,4,9], while possible antiaromaticity (although obviously reduced [7,8]) should lead to high and varied, essentially unpredictable (for example, see Ref. [9]), reactivity, especially toward nucleophiles.

The present article deals with the synthesis of novel substituted 1,3,2,4-benzodithiadiazines in both the hydrocarbon and fluorocarbon series for further investigation of this type of heteroatom reac-

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*Part XII of the series "Cyclic Aryleneazachalcogenenes"; part XI: Ref. [1], part X: Ref. [2].

Tribute to the memory of Professor Georg G. Yakobson (1928–1984).

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tivity as a new promising field of contemporary polysulfur-nitrogen heteroatom chemistry [10,11] (Scheme 1).

RESULTS AND DISCUSSION

Hydrocarbons

Precursors. The starting materials Ar-N=S=N-$SiMe_3$ (**25–41**, Scheme 2) were synthesized by a general method [12] from Ar-N=S=O and $LiN(SiMe_3)_2$. The useful improvement was the use of hexane as the solvent instead of Et_2O in the preparation of **28**, **29**, **31–34**, **36–39**; in Et_2O, the corresponding Ar-N=S=O compounds were mainly condensed into $(Ar\text{-}N=)_2S$ [12,13].

Cyclization. The 1:1 condensation of C_6H_5-N=S=N-$SiMe_3$ with SCl_2, followed by intramolecular electrophilic ortho-cyclization of the [C_6H_5-N=S=N-S-Cl] intermediate, had previously been used to prepare **1** [3]. Despite some limitations, the same approach also makes it possible to obtain various carbocyclic substituted derivatives of **1** in moderate to good yields (Scheme 2, Table 1).

Thus, the target heterocycle formation proceeds smoothly with all the 2-RC_6H_4-N=S=N-$SiMe_3$ (R = CH_3, OCH_3, F, Cl, and CF_3) compounds tried to give the corresponding 5-R-substituted derivatives of **1**. In the case of 4-RC_6H_4-N=S=N-$SiMe_3$, the cyclization readily occurs with R = CH_3, Cl, whereas with R = OCH_3, F, CF_3, and NO_2, the expected 7-R-substituted derivatives of **1** are not found in the reaction mixtures. This is somewhat unexpected because the site of ring closure, *meta* to R, is the same for both 2-R- and 4-RC_6H_4-N=S=N-$SiMe_3$.

With 3-RC_6H_4-N=S=N-$SiMe_3$ (R = CH_3, OCH_3, F, Cl), the cyclization is highly regioselective leading exclusively (R = OCH_3, F) or predominantly (R = CH_3, Cl) to 6-R-substituted derivatives of **1**; the ratio of the major 6-R isomer to the minor 8-R one is 78:22 (R = Cl) and 72:28 (R = CH_3), as shown by ^{1}H NMR spectroscopy (the structure of the 6-CH_3 isomer **4** and of the 6-F isomer **12** has been confirmed by X-ray crystallography, see Figure 1). In the case of R = CF_3, the cyclization fails, probably due to an unfavorable situation for electrophilic ring closure involving distribution of effective charges, q_i, around the carbocycle perimeter.

An attempt to use for the cyclization a leaving group other than H, namely t-Bu, with starting material **41** (Scheme 2) was unsuccessful, contrary to known examples of related intramolecular chalcogen-nitrogen ring closures with concomitant cleavage of a C(Ar)–C(*t*-Bu) bond [14,15].

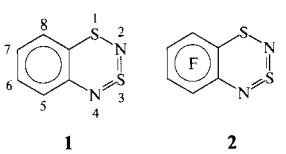
The preferred direction of cyclization of 3-RC_6H_4-N=S=N-$SiMe_3$ is consistent with the thermodynamics of corresponding Wheland-type σ-complexes (modeling a late transition state of an electrophilic aromatic substitution [16], Scheme 2) as well as factors of kinetic control for orbital-controlled El-Nu interaction [17]. Thus, according to the ΔH_f° (PM3) data, the 6-R isomer of a σ-complex is more stable than the 8-R one by ~3 kcal mol^{-1} (R = CH_3, Cl; 8-R isomer of a final product being observable) or by ~6 kcal mol^{-1} (R = OCH_3, F; 8-R isomer of a final heterocycle not being detectable). Under the orbital control, the site of the cyclization is determined by c_i^2 distribution for the Nu's HOMO [taken as aromatic ring part of the HOMO (PM3) of the (3-RC_6H_4-N=S=N-S-Cl) intermediate with El's LUMO being an S–Cl σ*-antibonding MO] with the c_6^2 value exceeding that of c_2^2 by a factor of 2.3–3.1 [18].

According to the ΔH_f° (PM3) data, there is no specific destabilization of the corresponding σ-complexes nor of the desired heterocyclic products in the case of the unsuccessful cyclizations as compared with the successful ones. It seems that a complex balance of different parameters of a molecular electronic structure (c_i^2 and q_i distribution, ε_i values of Nu's HOMO and El's LUMO) is responsible for the cyclization failures observed.

Molecular Structures. According to the X-ray diffraction data, the parent molecule **1** is planar within 0.066 Å [3], whereas heterocycle **2** is twisted along the $S^1 \ldots N^4$ line by 5.5° [4].

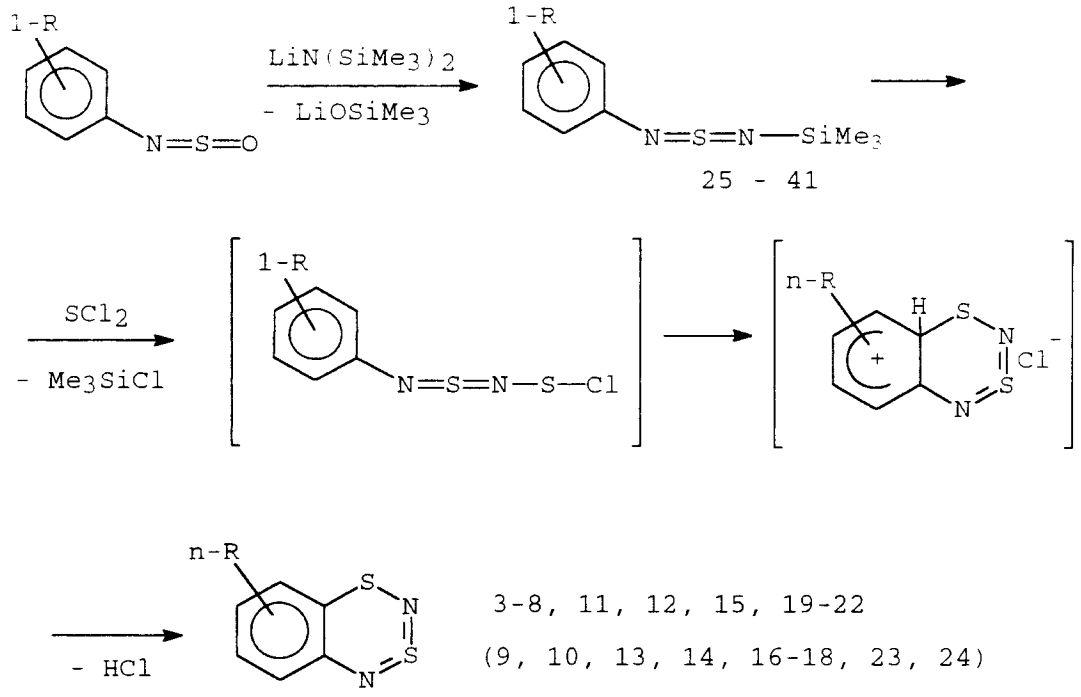
In the present work, both types of molecular geometry were observed (Figure 1, Table 2). In the case of derivatives of **1** possessing moderate or strong π-donor R substituents, **4** (R = 6-CH_3) and **7** (R = 5-OCH_3), the heterocycles were found to be bent along the $S^1 \ldots N^4$ line by 6.9 (1)° (**4**) or 10.8 (2)° (**7**) as the result of N^2 and S^3 deviation from the carbocycle plane to the same side by 0.204 (3) and 0.210 (3) Å (**4**) or 0.272 (6) and 0.314 (5) Å (**7**), respectively; the carbocycles themselves are planar within 0.025 (4) (**4**) or 0.014 (3) (**7**) Å.

Contrary to **4** and **7**, the heterocycles of derivatives of **1** with a weak π-donor and / or a strong σ-acceptor substituent R, **12** (R = 6-F) and **15** (R = 5-



1 **2**

SCHEME 1



SCHEME 2

Heterocycles:

n/R	CH_3	OCH_3	F	CF_3	Cl	NO_2
5	**3**	**7**	**11**	15	19	
6	**4**	**8**	**12**	(16)	20	
7	**5**	**(9)**	**(13)**	(17)	21	(23)
8	**6**	**(10)**	**(14)**	(18)	**22**	

5,7-Di(tert-butyl) derivative: **(24)**

Brackets indicate that corresponding heterocycle was neither synthesized by this way **(9, 13, 16–18, 23, 24)**, nor detected as minor isomer **(10, 14)**

Precursors:

1/R	CH_3	OCH_3	F	CF_3	Cl	NO_2
2	**25**	**28**	**31**	**34**	**37**	
3	**26**	**29**	**32**	**35**	**38**	
4	**27**	**30**	**33**	**36**	**39**	**40**

2,4,6-Tri(tert-butyl) derivative: **41**

CF_3) are planar within 0.054 (3) (**12**) or 0.009 (5) Å (**15**); the carbocycles are planar within 0.014 (5) (**12**) or 0.022 (5) Å (**15**). The interesting feature of **12** is the deviation of both S and N atoms from the carbocycle plane in opposite directions by −0.094 (**7**), −0.013 (9), 0.067 (8), and 0.056 (7) Å for S^1, N^2, S^3, and N^4, respectively. As a result, S^1 and N^2 lie below and S^3 and N^4 above the carbocycle plane, which makes the molecule somewhat propeller-like (the same conformation being adopted by **1** [3]).

The bond lengths (Table 2) in all compounds **4**, **7**, **12**, and **15** are typical [3,4,36]. It is worthwhile to note that in the $N^2=S^3=N^4$ fragment of the planar molecules **1** [3], **12**, and **15**, the bond lengths are nearly identical, whereas in the bent molecules, **2** [4], **4**, and **7**, they are markedly different.

The structural dichotomy of the title compounds is reminiscent of the result previously observed for related 3,7-R_2-1,5-dithia-2,4,6,8-tetrazocines: According to the X-ray diffraction data, with R = C_6H_5, the molecules are planar (and possess delocalized 10π-electron system), whereas with R = $(CH_3)_2N$, they are folded along an $S^1 \ldots S^5$ axis [19]. The distortion was rationalized as being driven by a pseudo–Jahn-Teller instability [20] in the π-system, namely, by π-donor-induced mixing of the high-lying π-HOMO with a low-lying virtual σ-MO [21]. It seems that the same explanation is also valid in the case of the title compounds. For verification, quantum chemical calculations are planned for the future.

Spectral Properties. The most interesting feature of ^1H (see also Ref. [3]), ^{13}C, and ^{19}F NMR spec-

TABLE 1 Characterization of the Compounds

Compound	*M.p.* (°*C*), *B.p.* (°*C*/*mm*)	*Yield* (*%*)	*Formula*	*MS* M^+ (*m*/*z*) *Measured* (*calculated*, ^{35}CL)
3	46–47	15	$C_7H_6N_2S_2$	181.9969 (181.9972)
4	70–71	30	$C_7H_6N_2S_2$	181.9969 (181.9972)
5	67–68	19	$C_7H_6N_2S_2$	181.9971 (181.9972)
7	73–74	41	$C_7H_6ON_2S_2$	197.9909 (197.9921)
8	31–32	25	$C_7H_6ON_2S_2$	197.9918 (197.9921)
11	73–74	42	$C_6H_3FN_2S_2$	185.9739 (185.9722)
12	63–64	56	$C_6H_3FN_2S_2$	185.9723 (185.9722)
15	85–86	38	$C_7H_3F_3N_2S_2$	235.9690 (235.9690)
19	97–98	31	$C_6H_3ClN_2S_2$	201.9431 (201.9426)
20	77–78	30	$C_6H_3ClN_2S_2$	201.9419 (201.9426)
21	111–113	18	$C_6H_3ClN_2S_2$	201.9393 (201.9426)
25	76–77/2	75	$C_{10}H_{16}N_2SSi$	224.0806 (224.0803)
26	98–99/3	46	$C_{10}H_{16}N_2SSi$	224.0808 (224.0803)
28	95–97/2	65	$C_{10}H_{16}N_2OSSi$	240.0755 (240.0753)
29	116–117/2.5	70	$C_{10}H_{16}N_2OSSi$	240.0747 (240.0753)
30	139–140/3.5	67	$C_{10}H_{16}N_2OSSi$	240.0752 (240.0753)
31	62–63/1	85	$C_9H_{13}FN_2SSi$	228.0549 (228.0553)
32	60–61/1	65	$C_9H_{13}FN_2SSi$	228.0552 (228.0553)
33	80–81/1	90	$C_9H_{13}FN_2SSi$	228.0552 (228.0553)
34	85–86/1	80	$C_{10}H_{13}F_3N_2$ SSi	278.0525 (278.0521)
35	82–84/1	30	$C_{10}H_{13}F_3N_2SSi$	278.0515 (278.0521)
36	77–78/1	70	$C_{10}H_{13}F_3N_2SSi$	278.0523 (278.0521)
37	109–110/3	58	$C_9H_{13}ClN_2SSi$	244.0249 (244.0257)
38	110–111/2	37	$C_9H_{13}ClN_2SSi$	244.0261 (244.0257)
39	111–112/3	50	$C_9H_{13}ClN_2SSi$	244.0240 (244.0257)
41	62–63	85	$C_{21}H_{38}N_2SSi$	321.1820 (321.1821)[a]
43		70	$C_8H_9F_4N_3S_2Si$	314.9932 (314.9943)
44	37–38	50	$C_8H_9ClF_3N_3S_2Si$[c]	331 (331)
47	62–63/1	36	$C_8H_9F_4N_3SSi$[c]	
48	134–135	85[b]	$C_{12}H_4F_8N_2S_2$	391.9698 (391.9688)
49	71–73	80	$C_{12}H_{10}F_2N_2S_2$	284.0252 (284.0253)
50	55–57/6	~100	C_5ClF_4NS[c]	
51	60–62/2	85	$C_5Cl_2F_3NS$[c]	
52	77–78/16	80	$C_5F_4N_2OS$[c]	
53	82–84/1	18	$C_{11}H_{18}F_4N_2SiSn$[c]	
55	136–138	34	$C_{10}H_4F_6N_2$	266.0269 (266.0269)
56	260–261	33	$C_{12}H_4F_6N_2$	290.0276 (290.0279)
57	64–65/1	80	$C_9H_{12}F_2N_2SSi$	264.0463 (264.0459)

[a](M^+ − *t*-Bu) peak.
[b]Both hydrolysis and reduction gave practically the same yield.
[c]Elemental analysis, found (calculated), %: **44:** C, 28.8 (29.0); H, 2.6 (2.7); F, 17.5 (17.2); N, 12.5 (12.7), S, 19.1 (19.3), Cl, 10.7 (10.7); **47:** C, 34.0 (33.9); H, 3.5 (3.2); F, 26.9 (26.8); N, 14.6 (14.8); S, 11.5 (11.3); **50:** Cl, 16.0 (16.3); **51:** C, 25.8 (25.6); F, 24.7 (24.4); N, 6.1 (6.0); S, 13.8 (13.7); Cl, 30.5 (30.3); **52:** C, 28.6 (28.3); F, 35.6 (35.8); N, 13.4 (13.2); S, 15.2 (15.1); **53:** C, 32.9 (32.9); H, 4.4 (4.5); F, 19.1 (19.0); N, 7.0 (7.0).

tra of the heterocycles synthesized is the enhanced shielding of the nuclei attached to $C^{5,8}$ as compared to those attached to $C^{6,7}$ (Table 3). This feature makes it possible, in particular, to assign unambiguously the signals of 6-R and 8-R isomers in the ^{1}H NMR spectra of the corresponding reaction mixtures.

In the ^{15}N NMR spectra of the title compounds, δ^{15}N values lie inside a relatively narrow range, ~280–250 ppm, demonstrating weak dependence upon the substituent R's both with respect to position and character (Table 3). The only exception is the polyfluorinated derivative 2 with δ^{15}N values of ~255 and ~233 [8]. Comparison of data collected for 5-R-derivatives of **1** on the one hand and for 6-, 7- and 8-R-derivatives on the other hand makes it possible to speculate that, in the latter case, the doublet (Table 3) refers to N^4 with a spin–spin coupling constant being $^3J(N^4–H^5)$, while the singlet refers to N^2.

It is interesting to note that the δ^{15}N range for the 12π-electron compounds under consideration lies between those deserved for related 10π-electron 2,1,3-benzothiadiazoles (~330–305) and 14π-electron 1,3,5,2,4-benzotrithiadiazepines (~250–240) [2,8]. Comparison of the title compounds with acy-

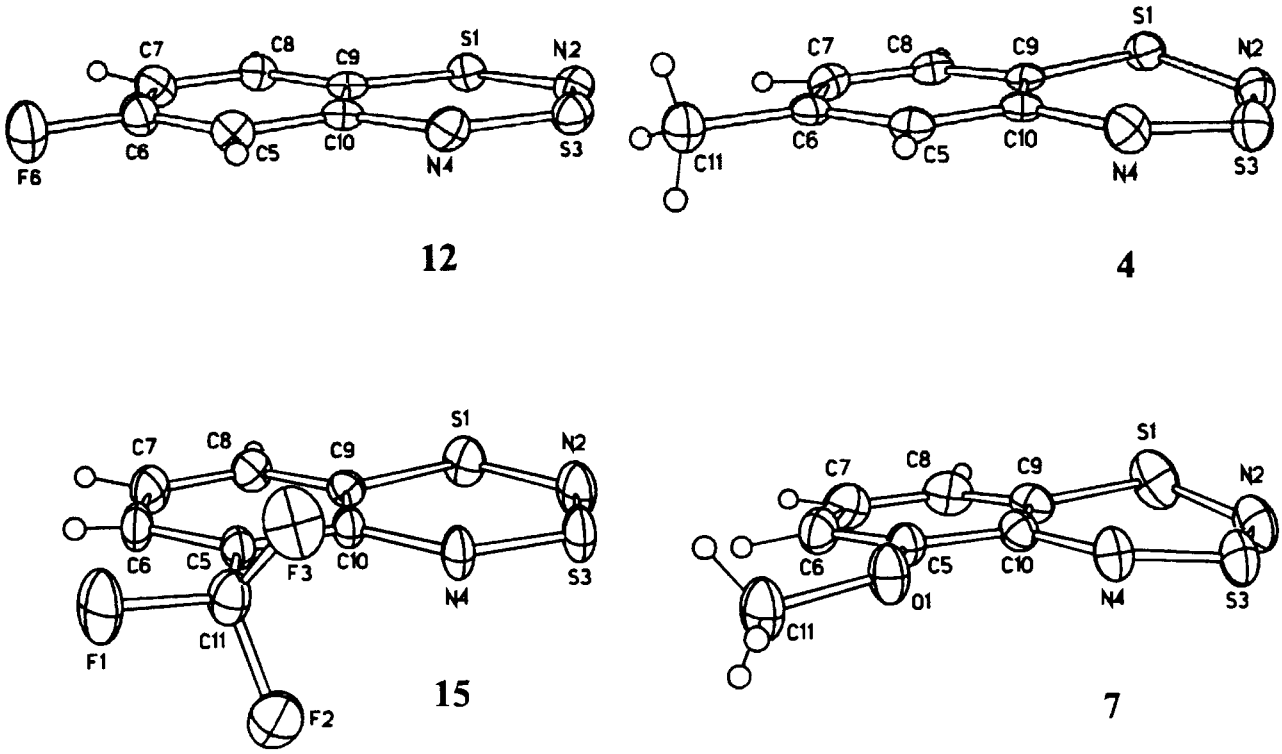


FIGURE 1 Molecular structure of compounds **4, 7, 12,** and **15.** For selected bond lengths and bond angles, see Table 2.

TABLE 2 Selected Bond Lengths (Å) and Bond Angles (°) in Molecules **4, 7, 12,** and **15**[a]

	4	7	12	15
C^9S^1	1.782(3)	1.780(3)	1.797(5)	1.786(5)
S^1N^2	1.675(4)	1.678(4)	1.673(4)	1.654(5)
N^2S^3	1.550(4)	1.544(3)	1.534(4)	1.537(5)
S^3N^4	1.520(3)	1.525(2)	1.531(5)	1.528(4)
N^4C^{10}	1.418(5)	1.415(3)	1.425(6)	1.412(6)
$C^{10}C^9$	1.400(5)	1.394(4)	1.405(6)	1.404(7)
$C^9S^1N^2$	106.0(2)	106.6(1)	105.3(2)	106.6(2)
$S^1N^2S^3$	122.1(2)	121.6(2)	124.3(3)	123.2(3)
$N^2S^3N^4$	119.6(2)	119.6(2)	119.0(2)	119.5(3)
$S^3N^4C^{10}$	123.3(3)	123.3(2)	123.3(3)	123.1(4)
$S^1C^9C^{10}$	123.9(3)	123.2(2)	124.1(4)	123.4(4)
$N^4C^{10}C^9$	123.7(3)	123.9(2)	123.7(5)	124.2(4)

[a]For atom numbering, see Figure 1.

clic analog Ph-S-N = S = N-Ph (δ^{15}N: ~329 and ~265 [8]) shows that sulfur–nitrogen ring closure affects strongly the magnetic shielding of only one nitrogen nucleus.

Another interesting feature of the title compounds is the presence of low-lying excited states (see also Refs. [3,4]). The long-wave absorption maxima in UV/Vis spectra are found in the range of ~620–635 nm (Ph-S-N = S = N-Ph: λ_{max} 434 nm [22]), again with weak dependence upon position and character of the substituent R (Table 3). In the consecutive range of related 10-, 12-, and 14π-electron heterocycles noted earlier, it sharply violates the monotonous correlation of λ_{max} with the number of π-electrons [2–4,8].

Fluorocarbons

The CsF-induced intramolecular nucleophilic ortho-cyclization of C_6F_5-S-N = S = N-$SiMe_3$ had previously been used to prepare **2** [4]. However, in the case of 2-$C_{10}F_7$-S-N = S = N-$SiMe_3$ (**42**; 2-$C_{10}F_7$: 1,3,4,5,6,7,8-heptafluoronaphth-2-yl), sulfur–nitrogen chain

TABLE 3 Spectral Data of the Compounds

Compound	NMR[a], δ			UV/Vis[b], λ_{max} (*nm*)	
	^{1}H	^{13}C	^{15}N (*J, Hz*)	^{19}F	(*log* ε)
3	6.66, 6.50, 5.61, 1.79	137.3, 132.7, 132.3, 131.4, 121.8, 115.0, 15.8	268.4 (s), 261.3 (s)		629 (2.60), 383 (3.29), 296 (4.13), 288 (4.16)
4	6.60, 5.76, 5.69, 1.98	140.6, 138.2, 133.1, 124.1, 123.9, 111.7, 20.3	269.4 (s), 263.0 (d, 2.7)		632 (2.61), 375 (3.18), 305 (4.12), 280 (4.14)
5	6.40, 5.80, 5.61, 1.98	143.9, 136.2, 130.3, 124.9, 123.0, 114.8, 20.8	263.1 (d, 3.0), 262.6 (s)		621 (2.69), 375 (3.16), 297 (4.16), 289 (4.16)
6	6.52, 6.42, 5.62, 1.61	137.7, 135.1, 132.8, 129.1, 120.6, 114.3, 15.8	261.7 (s), 260.0 (d, 3.0)		
7	6.71, 6.28, 5.34, 3.65	149.5, 133.3, 127.9, 116.3, 115.7, 114.7, 55.6	263.6 (s), 251.0 (s)		637 (2.63), 406 (3.48), 294 (4.00)
8	6.30, 5.73, 5.60, 3.61	161.3, 139.4, 124.8, 115.7, 111.0, 105.5, 55.1	274.9 (s), 261.2 (d, 2.7)		636 (2.49), 378 (3.19), 291 (4.15)
11	6.70, 6.38, 5.53	152.1, 133.3, 126.9, 119.4, 119.0, 116.4	268.0[c]	36.4	620 (2.66), 373 (3.43), 286 (4.29), 279 (4.31)
12	6.48, 5.76, 5.71	163.9, 140.2, 124.9, 118.4, 111.4, 110.1	275.7 (d, 2.2), 259.6 (s)	50.5	631 (2.56), 371 (2.97), 293 (4.14), 285 (4.16)
15	6.88, 6.84, 5.94	137.4, 132.4, 127.6, 127.3, 123.0, 120.8, 116.5	280.7 (s), 253.2 (s)	105.1	634 (2.64), 370 (sh), 293 (4.23), 285 (4.23)
19	6.65, 6.65, 5.64	135.7, 132.9, 131.8, 128.3, 122.2, 117.2	275.0 (s), 252.0 (s)		636 (2.74), 389 (3.26), 300 (4.25), 293 (4.26)
20	6.74, 5.90, 5.71	139.4, 135.7, 132.2, 124.7, 123.2, 113.7	272.8 (s) 259.0 (d, 2.5)		629 (2.60), 376 (3.06), 297 (4.31), 288 (4.34)
21	6.56, 5.82, 5.79	138.0, 136.9, 129.8, 124.1, 123.9, 117.1	264.5 (s), 260.2 (d, 2.4)		629 (2.71), 376 (3.14), 296 (4.34), 289 (4.33)
22	6.59, 6.41, 5.61	138.8, 133.2, 130.4, 129.4, 121.4, 115.0	261.6 (s), 251.2 (d, 2.0)		
25	7.86, 7.00–6.86, 2.19, 0.17				352 (3.88)
26	7.48, 7.34, 7.05, 6.80, 2.15, 0.12				346 (3.78)
28	7.42, 7.03, 6.88–6.79, 3.64, 0.12				373 (3.72)
29	7.34, 7.17, 7.08, 6.62, 3.55, 0.14				346 (3.95)
30	7.91, 6.70, 3.54, 0.20				370 (3.96)
31	7.73, 7.16–7.06, 0.17			43.7	345 (3.76)
32	7.56, 7.29, 7.09, 6.75, 0.16			50.7	340 (3.75)
33	7.87, 7.02, 0.31			49.5	348 (4.05)
34	7.77, 7.73, 7.57, 7.30, 0.25			100.8	343 (3.80)
35	8.01, 7.76, 7.36, 7.33, 0.21			99.1	337 (3.79)
36	7.78, 7.70, 0.37			100.1	350 (3.94)
37	7.75, 7.52, 7.30, 7.14, 0.30				347 (3.73)
38	7.66, 7.42, 7.09–6.99, 0.16				341 (3.71)

TABLE 3 (*Continued*)

Compound	NMR[a], δ			UV/Vis[b], λ_{max} (nm)	
	^{1}H	^{13}C	^{15}N (*J, Hz*)	^{19}F	(*log ε*)
39	7.65, 7.34, 0.39	144.5, 132.3, 129.1, 126.6, 1.6			351 (4.22)
41	7.32, 1.42, 1.29, −0.08				414 (2.10)
43	0.35			72.0, 25.5	354 (4.14)
44	0.34			88.5, 74.0, 24.9	358 (4.17)
47	0.16			71.5, 15.9	
48	4.47			29.6, 10.3, 2.0, −9.9	348 (3.85)
49	7.03, 6.39, 6.27, 4.45	165.3, 150.3, 138.7, 113.6, 105.3, 101.5		56.6	
50				74.0, 29.8	
51				90.5, 75.9, 30.0	
52				73.8, 19.0	326 (2.89)
53	0.41, 0.18			68.5, 12.3	
55	3.83			14.3, 11.5, 9.1, 4.9, 1.2, 0.2	350 (3.76)
56	2.60			17.2, 16.8, 12.2, 7.1, 4.4, 3.4	330 (3.78)
57	8.05–6.84, 0.15			45.3	340 (3.83)

[a]In $CDCl_3$; **25, 26, 29, 30, 39:** neat liquid: **35:** CCl_4.
[b]In $CHCl_3$; **25, 26, 30, 35, 38, 41:** heptane.
[c]Both N^2 and N^4 gave the same signal.

shortening occurred during the cyclization to give isomeric thiadiazoles instead of the expected dithiadiazines [23]. In this work, an attempt was made to extend this approach to polyfluoropyridine derivatives.

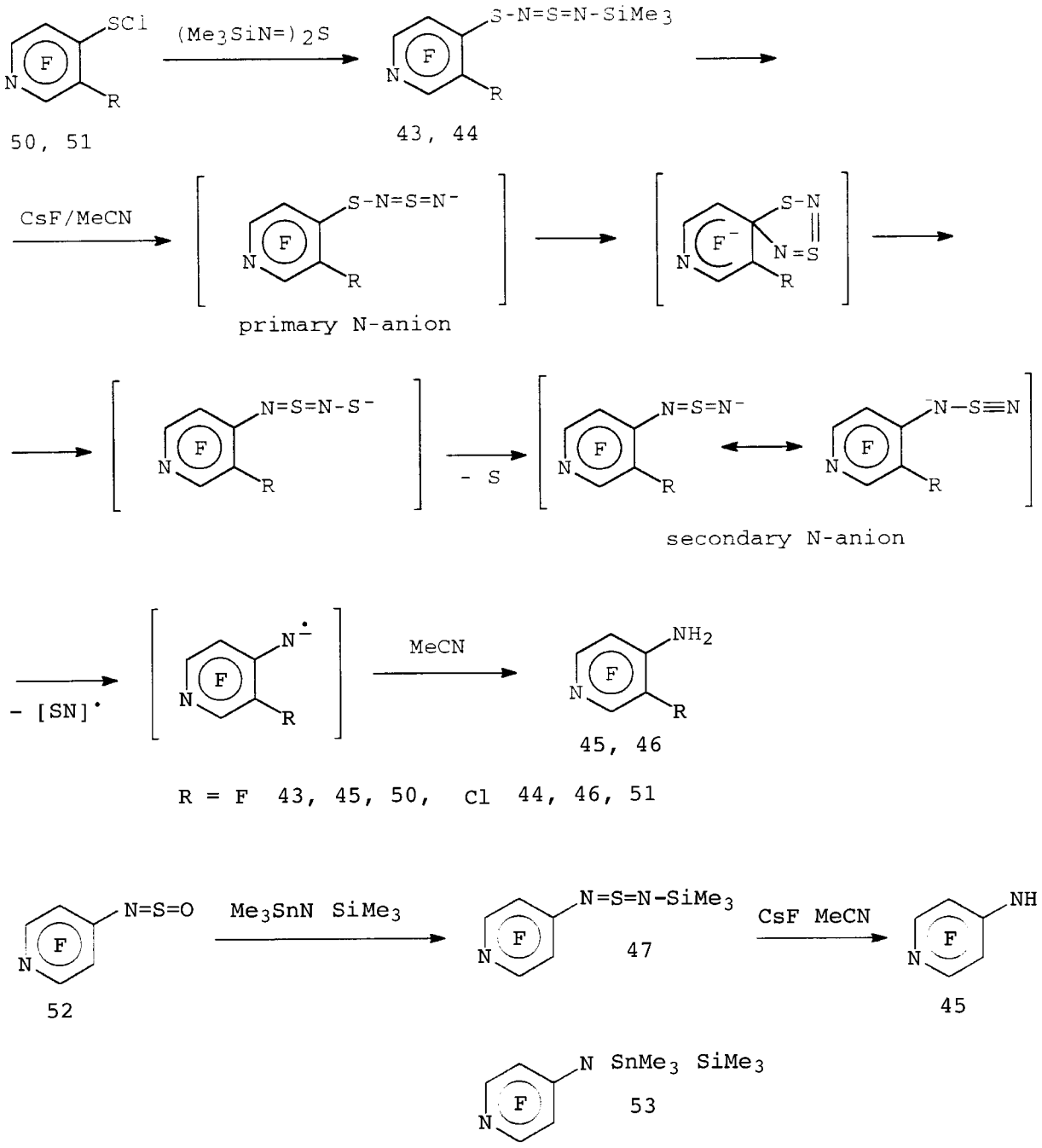
It was found that compounds **43** and **44**, when treated with CsF in boiling MeCN, were transformed into polyfluorinated aminopyridines **45** and **46**, respectively (Scheme 3). Despite the fact that no heterocycles were obtained, the important feature of the cyclization of **42** was reproduced; namely, the amine nitrogen of the final products **45** and **46** has occupied the position of the S(II) atom of the starting materials **43** and **44**. As a consequence, one can explain the transformations of **43** and **44** under the action of CsF in the same way (Scheme 3) suggested previously [23] for **42**. The only difference is that the nucleophilicity of even the secondary N-anions in the case of **43** or **44** is not enough to promote the intramolecular cyclization, and further transformations of the anions include complete degradation of a sulfur–nitrogen chain (Scheme 3). The results of control experiments with compound **47** (the direct precursor of the Scheme 3 secondary N-anion) are in agreement with these assumptions.

Thus, the present work provides additional evidence in favor of the previously suggested [23] mechanism involving a heteroatom chain shortening in the case of sulfur–nitrogen anions generated from Ar_F-S-N=S=N-$SiMe_3$ by the action of CsF in MeCN. On the whole, the previous data indicate clearly the relatively low nucleophilicity of the corresponding Ar_F-X-N=S=N^- (X = −; S) anions.

Heteroatom Reactivity

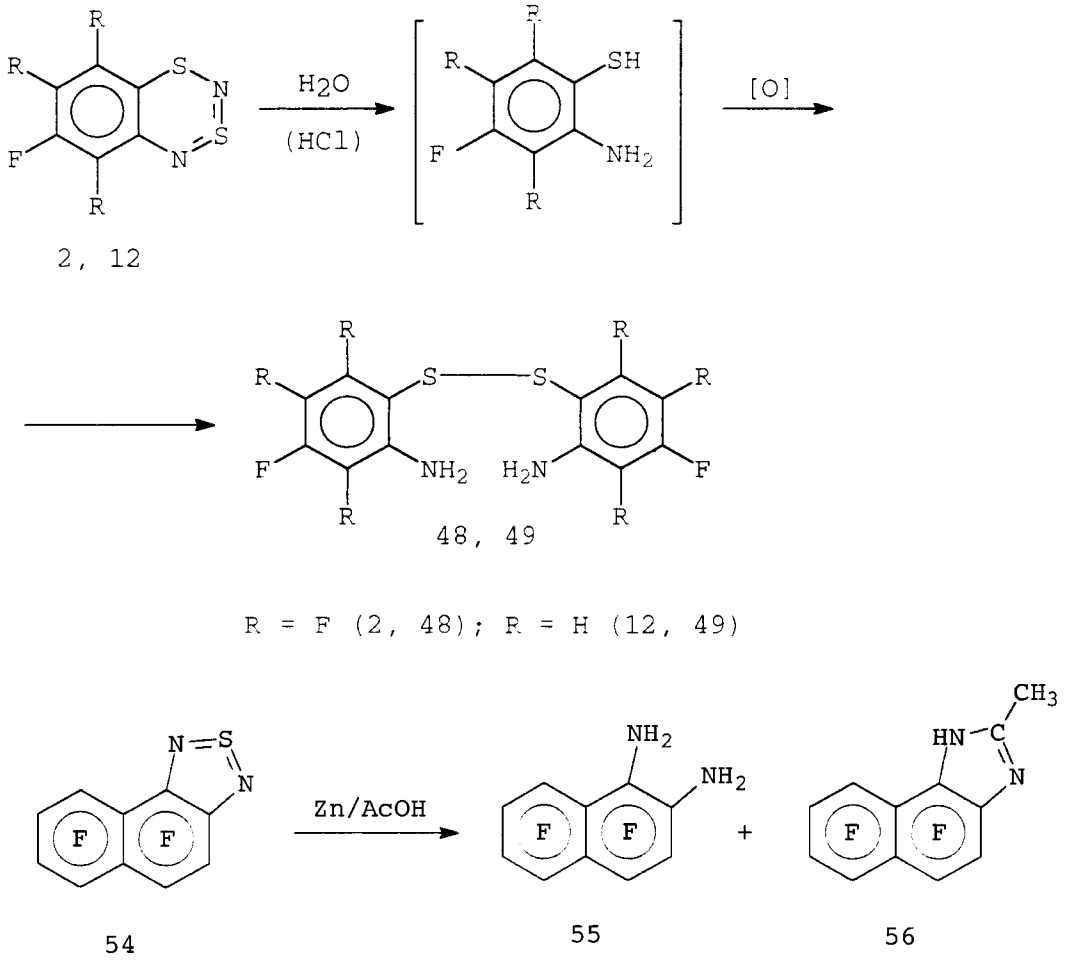
Although the heteroatom reactivity of the title compounds seems to be unpredictable on the whole (for example, see Ref. [9]), there is at least one obvious reaction, namely, hydrolysis to the corresponding 2-aminobenzenethiols. This is a useful adjunct to previously known methods for the preparation of ring-substituted 2-aminobenzenethiols involving the Herz reaction [24,25], reduction of ortho-nitro disulfides [26–28], hydroxide-mediated ring opening of 2-aminobenzothiazoles [29–31], the Newman procedure (i.e., the conversion of phenols to thiophenols via dialkylthiocarbamates) [31–33], and cleavage of benzothiazoles with hydrazine [34].

In principle, all the 1,3,2,4-benzodithiadiazines could be transformed into the corresponding 2-aminobenzenethiols. Actually, only two were so converted, just to provide examples. Thus, on acid catalyzed hydrolysis, compound **2** afforded polyfluorinated 2-aminobenzenethiol, identified for



technical reasons in the form of the corresponding disulfide **48** (Scheme 4; the same result was obtained by reduction of **2** with $NaBH_4$). In a similar way, hydrolysis of **12** gave the previously not described compound **49** (Scheme 4).

Thus, the cyclizations under consideration, followed by hydrolysis of the heterocycles, can be considered to be a useful method for both *ortho-thiolation* of benzeneamines in the hydrocarbon series and *ortho-amination* of benzenethiols in the fluorocarbon series (cf. also the related approach to *ortho-amination* of polyfluoroaromatic amines via polyfluorinated 2,1,3-benzothiadiazoles [35] and naphtho[1,2-c][1,2,5]thiadiazoles (Scheme 4).



SCHEME 4

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded with a Bruker DRX-500 spectrometer at frequencies of 500.13, 125.76, and 50.68 MHz, respectively, with TMS and NH_3 (liq.) as standards; the ^{19}F NMR spectra were measured on a Bruker AC-200 spectrometer at a frequency of 188.28 MHz with C_6F_6 as standard; the mass spectra were taken on a Finnigan MAT MS-8200 instrument (EI, 70 eV); and the UV/Vis spectra were collected on Beckman DU-8 or Specord M40 spectrophotometers.

The X-ray structure determinations (Table 4) were carried out on a Syntex $P2_1$ diffractometer using Cu-K_α radiation with a graphite monochromator. Corrections for both a systematic intensity drop and absorption were made. The structures were solved by direct methods using the SHELX-86 program and refined by the least-squares method in the full-matrix anisotropic (isotropic for H atoms) approximation using the SHELXL-93 and SHELXL-97 programs.

The PM3 calculations were performed with full geometry optimization using the MNDO-92 program [37].

Compounds **27** and **40** were reported earlier [12]. All hydrocarbon ArN=S=O compounds were prepared by a general method [38,39] from the corresponding $ArNH_2$ and $SOCl_2$ and characterized by high-resolution MS and multinuclear NMR spectroscopy.

The syntheses described subsequently were carried out in an argon atmosphere (except for **50** and **51**) in absolute solvents with stirring. The reagents were added dropwise, and the solvents were distilled off under reduced pressure. CsF was calcinated and SCl_2 was distilled directly before use. Tables 1 and 3 list the physical and analytical data for the compounds synthesized.

TABLE 4 Crystal and Refinement Data of Compounds **4, 7, 12,** and **15**[a]

	4	***7***	***12***	***15***
Formula	$C_7H_6N_2S_2$	$C_7H_6N_2OS_2$	$C_6H_3FN_2S_2$	$C_7H_3F_3N_2S_2$
M	182.26	198.26	186.22	236.23
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	6.553(1)	8.973(2)	3.889(3)	7.539(3)
b (Å)	7.237(1)	12.562(3)	5.731(4)	14.366(5)
c (Å)	9.622(2)	7.847(2)	15.927(13)	7.988(3)
α (°)	93.85(3)	90	81.98(6)	90
β (°)	108.08(3)	109.08(2)	86.65(6)	92.93(3)
γ (°)	113.42(3)	90	85.11(6)	90
V (Å^3)	388.4(1)	835.9(3)	349.8(5)	864.0(6)
Z	2	4	2	4
D_c (g cm^{-3})	1.558	1.575	1.768	1.816
μ (mm^{-1})	5.622	5.371	6.475	5.746
F(000)	188	408	188	472
Crystal size (mm)	0.06 × 0.12 × 0.45	0.08 × 0.55 × 1.5	0.05 × 0.50 × 12.0	0.06 × 0.16 × 1.9
Scan mode	θ–2θ	θ–2θ	θ–2θ	θ–2θ
2θ range (°)	<140	<140	<115	<140
Reflexions measured	1224	1536	946	1633
Observed $F_0 > 4\sigma_F$	917	1240	722	987
Transmission	0.69–1.74[b]	0.095–0.728	0.032–0.465	0.39–1.00
R (observed)	0.0475	0.0501	0.0633	0.0693
wR_2 (all data)	0.1252	0.1381	0.1593	0.1939
Goodness of fit	1.033	1.038	1.094	1.038

[a]Atomic coordinates, thermal parameters, bond lengths, and bond angles have been deposited at the Cambridge Crystallographic Data Centre.
[b]DIFABS program correction.

1-Aryl-3-trimethylsilyl-1,3-diaza-2-thiaallenes (**25**, **26**, **28–39**, **41**, **57**)

A solution of 0.06 mol of the corresponding ArNSO in 25 mL of Et_2O (hexane in the preparation of **28**, **29**, **31–34**, **36–39**, **57**) was added to a suspension of 10.0 g (0.06 mol) of $LiN(SiMe_3)_2$ in 50 mL of the same solvent at −30°C. During 2 hours, the temperature was raised to 20°C, and 6.6 g (0.06 mol) of Me_3SiCl in 10 mL of the same solvent was added. The precipitate was filtered off, the solvent distilled off, and the residue distilled in vacuo (**25**, **26**, **28–39**, **57**; orange-red oils) or recrystallized from hexane (**41**, orange-yellow crystals).

Substituted 1,3,2,4-Benzodithiadiazines (**3–8**, **11**, **12**, **15**, **19–22**)

Solutions of 1.03 g (0.01 mol) of SCl_2 and 0.01 mol of Ar-N=S=N-SiMe$_3$ (**25–29**, **31**, **32**, **34**, **37–39**), each in 30 mL of CH_2Cl_2, were slowly mixed by adding them dropwise to 300 mL of CH_2Cl_2 at 20°C, over a period of 1 hour. After a further 1 hour, the reaction solution was filtered, the solvent distilled off, the residue sublimed in vacuo, and the product recrystallized from hexane. Compounds **3–5**, **7**, **8**, **11**, **12**, **15**, **19–21** were isolated as black crystals.

In the case of Ar = 3-RC_6H_4 (**26**, **29**, **32**, **38**), the reaction solution after filtration was concentrated to an appropriate volume, and the ^{1}H NMR spectrum was measured to estimate the ratio of 6-R and 8-R isomers. After complete evaporation of the reaction solution, followed by sublimation of the residue, the ^{1}H NMR and mass spectra of the sublimate were recorded to confirm (where it was necessary) the presence of two isomers in the same 6-R:8-R ratio. Then, the major 6-R isomer was obtained by recrystallization, while the minor 8-R isomer (compounds **6** and **22**) was characterized only spectroscopically without eventual isolation.

In the case of the **30**, **33**, **35**, **36**, **40**, and **41** precursors under the same conditions as described earlier, only $(SN)_4$ was obtained along with some unidentified products.

2,3,5,6-Tetrafluoro-4-pyridine Sulfenylchloride (**50**) *and 3-Chloro-2,5,6-trifluoro-4-pyridine Sulfenylchloride* (**51**)

An excess of Cl_2 was passed through a solution of 0.02 mol of 4-Py$_F$SH [40] or its 3-Cl derivative [41] in 40 mL of CCl_4 at 20°C. The solvent was distilled off and the residue distilled in vacuo. Compounds **50** [40] and **51** were obtained as red oils.

1-(2,3,5,6-Tetrafluoropyrid-4-yl)-4-trimethylsilyl-2,4-diaza-1,3-dithia-2,3-butadiene (**43**) *and 1-(3-Chloro-2,5,6-trifluoropyrid-4-yl)-4-trimethylsilyl-2,4-diaza-1,3-butadiene* (**44**)

At 20°C, to a solution of 3.09 g (0.015 mol) of $(Me_3SiN=)_2S$ [23] in 25 mL of CH_2Cl_2 was added during 0.5 hour a solution of 0.015 mol of **50** or **51** in 10 mL of the same solvent. After 3 hours, the solvent was distilled off and the residue dissolved in hexane and passed rapidly through a short silica gel column under an elevated pressure of air. After eluate evaporation in vacuo, compound **43** was obtained as a yellow oil, and compound **44** as yellow crystals (from hexane).

1-(2,3,5,6-Tetrafluoropyrid-4-yl)-3-trimethylsilyl-1,3-diaza-2-thiaallene (**47**), *N-Sulfinyl-4-amino-2,3,5,6-tetrafluoropyridine* (**52**) *and N-Trimethylsilyl-N-trimethylstannyl-4-amino-2,3,5,6-tetrafluoropyridine* (**53**)

A mixture of 6.64 g (0.04 mol) of 4-Py_FNH_2 [42] and 10 mL of $SOCl_2$ was boiled until HCl evolution ceased. The solvent was distilled off, and the residue was distilled under reduced pressure. Compound **52** was obtained as a yellow liquid.

At 20°C, to a solution of 9.72 g (0.03 mol) of $Me_3SnN(SiMe_3)_2$ [12] in 10 mL of MeCN was added a solution of 6.36 g (0.03 mol) of **52** in 10 mL of MeCN. After 0.5 hour, the solvent was distilled off, and the residue was twice distilled in vacuo. Compound **47** was obtained as an orange-yellow oil and compound **53** as a colorless liquid.

Transformations of Compounds **43**, **44**, *and* **47** *under the Action of CsF. 4-Amino-2,3,5,6-tetrafluoropyridine* (**45**) *and 4-Amino-3-chloro-2,5,6-trifluoropyridine* (**46**)

To a stirred suspension of 0.31 g (0.002 mol) of CsF in 50 mL of MeCN was added, during 0.5 hour, with boiling, a solution of 0.002 mol of **43**, **44**, or **47** in 10 mL of MeCN. The mixture was cooled to 20°C, filtered, the solvent distilled off, and the residue sublimed in vacuo and recrystallized from hexane. Compound **45** was obtained from both **43** and **47** [the yield in both cases was 0.30 g (90%)] and compound **46** from **44** [0.34 g (93%)]. The melting points, ^1H, and ^{19}F NMR spectra and mass spectra of **45** and **46** were identical to that of authentic samples [42, 43].

In the absence of CsF, compounds **43**, **44**, and **47** were recovered unchanged under the same conditions.

Acid Hydrolysis and Reduction of 5,6,7,8-Tetrafluoro-1,3,2,4-benzodithiadiazine (**2**). *2,2′-Diamino-3,3′,4,4′,5,5′,6,6′-octafluorodiphenyl Disulfide* (**48**)

At 0°C, to a solution of 0.48 g (0.002 mol) of **2** [4] in 10 mL of THF was added a solution of 0.36 g of 1:10 diluted hydrochloric acid in 5 mL of THF. After 0.5 hour, 15 mL of Et_2O and then aqueous Na_2CO_3 were added. The organic layer was separated, dried over $CaCl_2$, the solvent distilled off, and the residue recrystallized from heptane. Compound **48** was obtained as long yellow needles.

At 20°C, to a suspension of 0.23 g (0.006 mol) of $NaBH_4$ in 10 mL of THF was added a solution of 0.72 g (0.003 mol) of **2** [4] in 5 mL of THF. After 2 hours, the reaction mixture was diluted with 20 mL of H_2O, acidified with HCl, and extracted with Et_2O. After the usual workup of the extract, compound **48** was obtained in the form described earlier.

Acid Hydrolysis of 6-Fluoro-1,3,2,4-benzodithiadiazine (**12**). *2,2′-Diamino-4,4′-difluorodiphenyl Disulfide* (**49**)

Under the conditions described earlier for **2**, compound **49** was obtained from **12** as transparent yellow prisms (from hexane).

Reduction of 4,5,6,7,8,9-Hexafluoronaphtho[1,2-c][1,2,5]thiadiazole (**54**). *1,2-Diamino-3,4,5,6,7,8-hexafluoronaphthalene* (**55**) *and 2-Methyl-4,5,6,7,8,9-hexafluoro-1H-naphth[1,2-d]imidazole* (**56**)

A mixture of 2.94 g (0.01 mol) of **54** [23], 35 mL of AcOH, and 6.54 g (0.1 mol) of Zn powder was boiled during 4 hours, filtered, and poured into 350 mL of H_2O. The precipitate was filtered off, dried in air, and extracted with benzene. A benzene insoluble substance was sublimed in vacuo to give **56** as colorless crystals. The benzene extract was evaporated, and the residue was sublimed in vacuo to give **55** as colorless crystals.

The use of $NaBH_4$ under the conditions of Ref. [32] was unexpectedly unsuccessful.

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