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Interaction of 1,3λ⁴δ²,2,4-benzodithiadiazines with neutral and charged S-electrophiles: SCl_2, C_6F_5SCl, and NS_2^+

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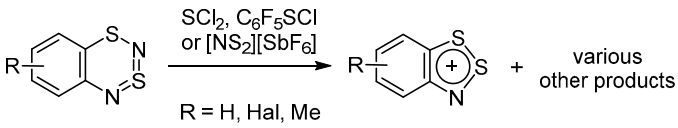


Reactions of 1,3λ⁴δ²,2,4-benzothiadiazines with SCl_2, C_6F_5SCl, and $[NS_2][SbF_6]$ leading to 1,2,3-benzodithiazolium salts (Herz salts) were investigated. The relative rate of reaction with SCl_2 significantly depends on the nature of the substituent and its position in the carbocycle. Halogen substituents Cl, Br, and I slow down the reaction, especially if located closely to the heterocycle (positions 5 and 8). In the case of C_6F_5SCl and R = H, chlorination of the carbocycle and opening of the heterocycle also takes place with the formation of 7-chloro-1,3λ⁴δ²,2,4-benzothiadiazine and C_6F_5–S–N=S=N–Ar (Ar = 2-Cl-6-$F_5C_6SC_6H_3$), respectively. In the reaction with NS_2^+, along with contraction of the heterocycle, also its expansion occurs with the formation of 1,2,4λ⁴δ²,3,5-benzotrithiadiazepine.

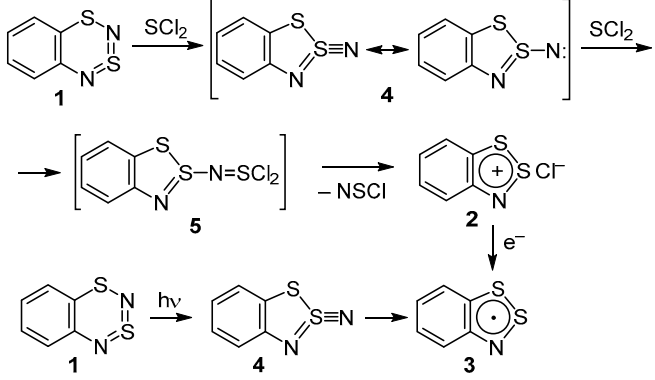
Keywords: benzodithiazolium salts, 1,3,2,4-benzothiadiazines, 1,2,4,3,5-benzotrithiadiazepine, dithionitronium, pentafluorobenzenesulfenyl chloride, sulfur dichloride, sulfur-nitrogen heterocycles, tetrasulfur tetranitride.

1,3λ⁴δ²,2,4-Benzothiadiazines **1** (the indices λ and δ are omitted below) are relatively little studied 12π-electron, i.e., formally antiaromatic, compounds which are stable at normal conditions. Their heteroatom reactivity is high, diverse, and largely unpredictable,[1–7] the ring contraction being the most typical kind. In particular, the reaction with SCl_2 leads to 1,2,3-benzodithiazolium salts **2** (Herz salts), which is the mildest method for their synthesis, allowing to obtain also otherwise unaccessible derivatives;[2c,3] the reaction with Ph_3P leads to iminophosphoranes Ph_3P=N–R (R = 1,2,3-benzodithiazol-2-yl);[1,4] thermolysis and photolysis of dilute solutions produces 1,2,3-benzodithiazolyls (Herz radicals) **3**.[1,3,5] At high concentrations, the thermolysis leads both to ring contraction toward 1,2,3-dithiazole or 1,2,5-thiadiazole ring and to ring expansion toward 1,2,4,3,5-trithiadiazepine and 1,3,2,4,7-dithiatriazepine ring.[1,6] The addition of H_2O causes opening of the heterocycle.[4b,7]

Herz salts **2** are preparative precursors of Herz radicals **3** which are stable π-radicals, and they can in some cases be isolated separately and used as structural blocks in the design and synthesis of molecular semiconductors and magnetics.[8] Recently, they have found application in the synthesis of polycyclic sulfur-nitrogen π-systems with intense absorption in the near-infrared range.[9] For the purpose of spectroscopic investigation, including reaction mechanism study, it is convenient to generate Herz radicals **3** from compounds **1**.[1,3,5]

The key intermediate of photolysis and likely also thermolysis of compounds **1** is singlet nitrenoid **4** detected under conditions of matrix isolation.[5c,10] It has been assumed that it also takes part in reaction of compounds **1** with PPh_3 and SCl_2 by oxidative imination of the P and S atoms of those reactants (Scheme 1).[1,2c] Isomerization of compounds **1** into intermediate **4** requires energy the source of which can be the interaction of the low-lying vacant

Scheme 1



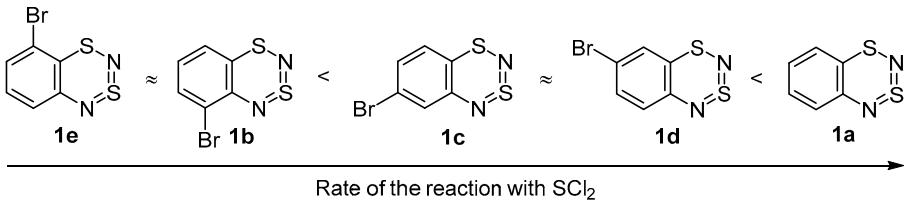


Figure 1. The effect of substituent in the carbocycle on the rate of reaction of compunds **1a**–**e** with SCl_2.

π-MO with the lone electron pair of phosphorus or sulfur atoms.[2c] In this context, compounds **1** act as Lewis acids, but PPh_3 и SCl_2 have the role of Lewis bases.

The results of reactions with other compounds, including sulfur compounds, is difficult to predict. The formation of new types of compounds, including new precursors of 1,2,3-benzodithiazolyl radicals, can be expected. In particular, the exchange of Cl atoms for organic groups in iminosulfurane **5** was expected to stabilize the latter, so that it would be possible to isolate such compounds and study their properties.

In the present work, the study of reactions of compounds **1** with SCl_2 is carried forward and other S-electrophiles, C_6F_5SCl and $[NS_2][SbF_6]$, are used for the first time. NS_2^+ cation possesses high and diverse reactivity. However, its reactions with heterocyclic compounds have been investigated only to a limited extent.[11]

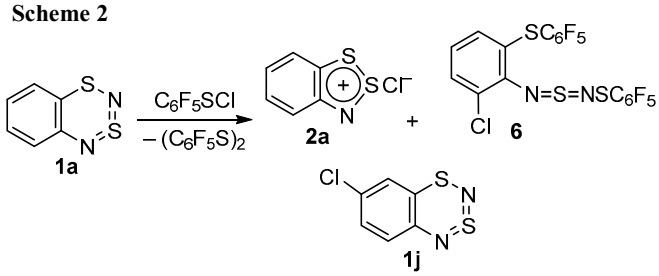
Previously it was found, using the method of competing reactions, that for derivatives of compound **1a**, containing halogens (I, Br) in 6 and 8 positions, the relative rate of their reaction with SCl_2 depends on the position of halogen: 8-isomers react more slowly.[2c] In the present work, the effect of the nature and position of substituents on the relative rate of this reaction is studied using the same method. The processes taking place in the reaction mixture are complex and not entirely understood.[2c] Therefore, it is possible to establish only qualitative relationships which nevertheless are important for the understanding the reactivity of 1,3,2,4-benzothiadiazines **1** and development of methods for their synthesis.

It was found that compounds **1b** (5-Br) and **1e** (8-Br) interact with SCl_2 at approximately equal rates which are significantly slower than in the case of compounds **1c** (6-Br) and **1d** (7-Br) the reaction rates of which, too, have similar values. Compound **1a** reacts faster than compounds **1c**,**d** (Fig. 1). Compound **1f** (8-Cl) is also more inert toward SCl_2 than its isomer compound **1g** (6-Cl), while between compounds **1h** (8-CH_3) and **1i** (6-CH_3) such difference is not observed. Therefore, Cl, Br, and I atoms have deactivating effect which becomes weaker with increasing their distance from the heterocycle, which corresponds to their inductive effect.

The deactivating effect of Cl, Br, I atoms better corresponds to the role of compounds **1** as nucleophiles, rather than Lewis acids. Meanwhile it can be not excluded that intermediate **4** also can act as nucleophile, since its stable analog $Ph_3S{\equiv}N$ is known to have such property.[12]

The reaction of compound **1a** with C_6F_5SCl leads to salt **2a** and $(C_6F_5S)_2$ as the main products. In addition to that, the chlorination of compound **1a** leading to the formation of compound **1j** (identified by ^{1}H NMR spectroscopy)[2b] and opening of the heterocycle leading to the formation of compound **6** (Scheme 2), the structure of which has been established using X-ray structural investigation (Fig. 2) are also observed. However, the low quality of crystals (*R* 0.17) prevents the discussion of bond lengths and valence angle values.

Scheme 2



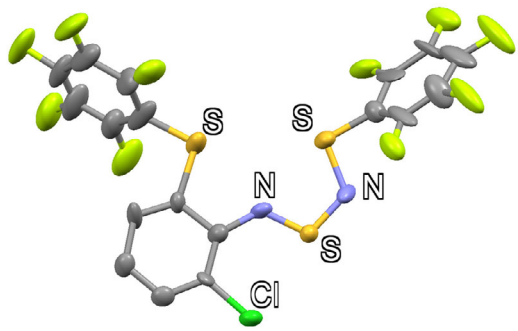


Figure 2. Molecular structure of compound **6** with atoms represented as thermal vibration ellipsoids of 50% probability.

The reaction of compound **1a** with C_6F_5SCl proceeds slower than with SCl_2, while $(C_6F_5)_2S_n$ (n = 1,* 2) do not interact with compound **1a** under these conditions. This speaks against the hypothesis about the reactions of compounds **1** with XSCl (X = Cl, C_6F_5) as oxidative imination of the S atom by nitrenoid **4** and in favor of the role of the latter reagents as S-electrophiles: the transition from X = Cl to X = C_6F_5 should not decrease the ability of the S to to be iminated, yet it decreases its electrophilicity; compounds $(C_6F_5)_2S_n$ (n = 1, 2) also should be amenable to imination, but they are not electrophiles. Still one further cause of different reactivity of the reagents under discussion is the presence or absence of a good leaving group in their molecules, namely Cl atom, the elimination

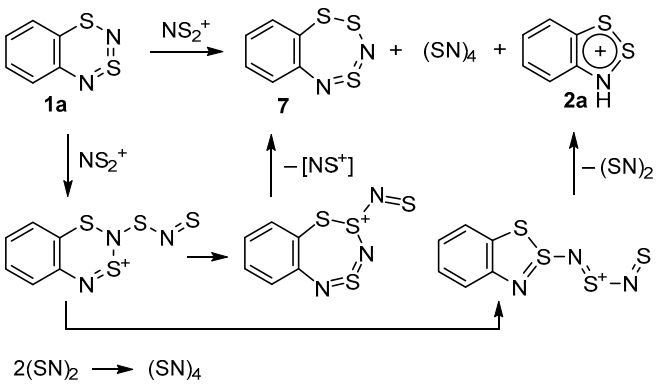
* In the present work, $(C_6F_5)_2S$ was synthesized by a new method using reaction of C_6F_5MgBr with $(SN)_4$. Although this method does not have significant advantages over those described before,[13] it is of interest to note that formation of organic sulfides in reaction of $(SN)_4$ with Grignard reagents was not observed previously.[14]

of which is necessary for conversion of the starting compounds into the final products.

Introduction of the C_6F_5S substituent into the carbocycle of compound **6**, which requires the C–S bond cleavage in either substrate or reagent, as well as substitution of H atom by Cl atom (taking place also upon formation of compound **1j**) are difficult to explain by electrophilic or nucleophilic substitution reactions. It can be suggested that radical cation of compound **1a** participates in the process, having been previously detected by ESR spectroscopy during electrochemical oxidation of compound **1a**.[15]

The reaction of compound **1a** with $[NS_2][SbF_6]$ leads to products of both ring contraction and ring expansion – 1,2,3-benzodithiazolium (**2a**) and 1,2,4,3,5-benzotrithiadiazepine (**7**), as well as $(SN)_4$ (Scheme 3). The formation of these compounds can be explained by electrophilic attack of cation NS_2^+ at N-2 atom of the substrate (in contrast to NO_2^+, the reaction center of NS_2^+ ion is S, not N atom)[11a] with subsequent bifurcation of the reaction path toward the elimination of either NS^+ or $(SN)_2$ further dimerizing into $(SN)_4$ (Scheme 3). It should be noted that the yield of compound **7** in this reaction (20%) is twice as high as in a previously published method of its synthesis (10%).[16]

Scheme 3



In summary, contraction, expansion, and opening of the heterocycle take place in the investigated reactions of 1,3,2,4-benzothiadiazines with S-electrophiles. The transformation of antiaromatic 1,3,2,4-dithiadiazine heterocycle into aromatic 1,2,3-dithiazolium is the most typical process. It is energetically favorable, which is the obvious driving force of the reaction. The reaction mechanisms are complex and require additional experimental and, especially, theoretical study because of the obvious difficulties of the experimental approach. Nevertheless, the obtained data allow to state that compounds XSCl (X = Cl, C_6F_5) in reactions with 1,3,2,4-benzothiadiazines act as electrophiles rather than Lewis bases.

Experimental

^{1}H NMR spectra were acquired on Bruker DRX-500 (500 MHz) and Bruker WP200-SY (200 MHz) spectrometers, and ^{13}C NMR spectra were acquired on a Bruker DRX-500 (126 MHz) spectrometer. ^{14}N NMR spectrum of the reaction mixture of compound **1a** with $[NS_2][SbF_6]$ was acquired on a Bruker DRX-500 (36 MHz) spectrometer. ^{19}F NMR spectra were acquired on Bruker DRX-500 (471 MHz) and Bruker WP200-SY (188 MHz) spectrometers. Chemical shift reference was TMS (for ^{1}H and ^{13}C nuclei), liquid NH_3 (for ^{14}N nuclei), C_6F_6 (for ^{19}F nuclei). High-resolution mass spectra were recorded on a Finnigan MAT MS-8200 spectrometer (ionization by electron impact at 70 eV). Electronic absorption spectra in UV and visible range were recorded on a Hewlett Packard 8453 spectrometer.

All described experiments were performed in absolute solvents under stirring in Ar atmosphere. Reagents were added dropwise. Solvents were evaporated under reduced pressure.

Compounds **1a**–**e**,[2a,c] **1j**,[2b] mixtures of compounds **1f** and **1g**, **1h** and **1i**[2b] and C_6F_5SCl[17] were obtained in accordance with the methods described earlier. Salt $[NS_2][SbF_6]$[18] was generously gifted by Dr. K. V. Shuvaev.

Competing reactions of 1,3,2,4-benzothiadiazines 1 with SCl_2. A solution of SCl_2 (10 mg, 0.1 mmol) in CH_2Cl_2 (0.2 ml) was added to a solution of 1:1 mixture of compounds **1b** and **1c**, **1b** and **1e**, **1c** and **1d**, **1c** and **1a**, **1f** and **1g**, **1h** and **1i** (0.2 mmol) in CH_2Cl_2 (1.5 ml). After 30 min, the solution was filtered, the filtrate was evaporated to dryness, the residue was sublimated *in vacuo*. According to ^{1}H NMR spectrum, compound **1g** was absent in the sublimate; in other cases the ratio of compounds was as follows: **1b**:**1c** > 10; **1b**:**1e** = 1:1; **1c**:**1d** = 1:1; **1c**:**1a** = 2:1; **1h**:**1i** = 1:1.

Interaction of 1,3,2,4-benzothiadiazine (1a) with C_6F_5SCl, synthesis of compound 6. Compound **1a** (84 mg, 0.5 mmol) in CH_2Cl_2 (1.5 ml) was added within 20 min to a solution of C_6F_5SCl (118 mg, 0.5 mmol) in CH_2Cl_2 (1.5 ml). After 1 week, the yellow fine crystalline precipitate of salt **2a** was filtered off. The filtrate was evaporated to dryness, the residue was separated by column chromatography on silica gel (eluent – hexane). $C_6F_5SSC_6F_5$ and compound **6** were isolated.

1,2,3-Benzodithiazolium chloride (2a). Yield 30 mg (32%), light-brown crystals, mp 145–160°C (decomp.). The ^{1}H NMR spectrum matched a published one.[19]

2-Chloro-6-[(pentafluorophenyl)sulfanyl]-*N*-({[(pentafluorophenyl)sulfanyl]imino}-λ^4-sulfanylidene)aniline (6). Yield 10 mg (3.5%), orange crystals, mp 126–129°C. UV spectrum (pentane), λ_{max}, nm (log ε): 432 (3.85), 361 (3.73), 223 (4.43). ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.31 (1H, dd, *J* = 8.0 *J* = 1.0, H Ar); 6.97 (1H, t, *J* = 8.0, H Ar); 6.79 (1H, d, *J* = 8.0, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 139.3; 131.2; 127.9 (CH); 127.1; 126.1 (CH); 126.5 (CH); signals of C_6F_5 groups were not detected due to their low intensity. ^{19}F NMR spectrum (471 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 32.3 (2F, d, *J* = 19.0); 31.1 (2F, d, *J* = 20.0); 14.7 (1F, tt, *J* = 21.0, *J* = 4.0); 13.1 (1F, t, *J* = 21.0); 3.19–3.04 (2F, m); 2.90–3.03 (2F, m). Found, *m*/*z*: 567.8987 $[M]^+$. $C_{18}H_3ClF_{10}N_2S_3$. Calculated, *m*/*z*: 567.8987.

Decafluorodiphenyl disulfide. Yield 40 mg (40%), pale-yellow crystals, mp 49–50°C (mp 50–51°C[20]).

Identification of 7-chloro-1,3,2,4-benzothiadiazine (1j) as a product of interaction of 1,3,2,4-benzothiadiazine (1a) with C_6F_5SCl. C_6F_5SCl (2.11 g, 0.009 mol) was added to a solution of compound **1a** (0.50 g, 0.003 mol) in CH_2Cl_2 (5 ml). After 2 days, the solution was filtered, the filtrate was evaporated, the residue was sublimated *in vacuo* (80°C, 2 Torr). The main signals in the ^1H NMR spectrum of the green sublimate (1.12 g) matched those of compound **1j**,[2b] while the main signals in the ^{19}F NMR spectrum matched those of decafluorodiphenyl sulfide.[20a]

Decafluorodiphenyl disulfide. A solution of C_6F_5Br (9.88 g, 40 mmol) in THF (20 ml) during 30 min was added to a refluxing suspension of Mg turnings (0.96 g, 40 mmol), activated by I_2, in THF (80 ml). Almost all Mg was dissolved within 30 min. Freshly recrystallized $(SN)_4$ (1.84 g, 10 mmol) was added to the reaction mixture in small portions. After 1.5 h, the mixture was cooled with ice water and a solution of Br_2 (3.20 g, 20 mmol) in THF (15 ml) was gradually added. After 30 min, the mixture was filtered, the solvent was evaporated, and the residue was extracted with boiling hexane (4×30 ml). The combined extract was evaporated, the residue was sublimated and recrystallized from hexane. The sublimation and recrystallization was repeated to obtain decafluorodiphenyl sulfide. Yield 3.18 g (48%), slightly yellow crystals, mp 86–88°C (mp 85–86°C[13c]). The ^{19}F NMR spectrum matched a published one.[21]

Interaction of 1,3,2,4-benzothiadiazine (1a) with $(C_6F_5)_2S_n$ (n = 1, 2). Compound **1a** (84 mg, 0.5 mmol) and $(C_6F_5)_2S_n$ (n = 1, 2) (183 or 199 mg, 0.5 mmol) were dissolved in $CDCl_3$ (0.7 ml). ^1H and ^{19}F NMR spectra were recorded right after the mixing and after keeping for 15 days at room temperature. Only signals of starting compounds were observed in the spectra.

Interaction of 1,3,2,4-benzothiadiazine (1a) with $[NS_2][SbF_6]$. $[NS_2][SbF_6]$ salt (166 mg, 0.52 mmol) was added in small portions to a solution of compound **1a** (89 mg, 0.52 mmol) in CH_2Cl_2 (40 ml). After 16 h, the black precipitate (78 mg) was filtered off and washed on the filter with CH_2Cl_2. The filtrate was evaporated, the residue was dissolved in $CDCl_3$ (62 mg of black substance remained), and NMR spectra were recorded. The ^1H NMR spectrum corresponded to a 1:3 mixture of compounds **1a**[2a] and **7**,[16] in the ^{14}N NMR spectrum, beside signals of compounds **1a**[2c] and **7**,[16] an intensive signal at 125 ppm was observed corresponding to $(SN)_4$.[22] Signals of cations of salt **2a** were absent in the spectra. Chromatography on silica gel (eluent PhH–heptane, 1:1, with addition of 1% EtOAc) separated compound **7** and $(SN)_4$. The insoluble in $CDCl_3$ black substance was dissolved in CF_3CO_2H and ^1H NMR spectrum was recorded containing signals of cations of salt **2a** and NH_4^+ in 12:1 molar ratio.

1,2,4$\lambda^4\delta^2$,3,5-Benzotrithiadiazepine (7). Yield 19.3 mg (18%, 20% considering the incomplete conversion of compound **1a**), red crystals, mp 27–28°C. The ^1H NMR spectrum matched a published one.[16]

Tetrasulfur tetranitride ($(SN)_4$). Yield 4.5 mg (9%), orange crystals, mp 180–190°C (decomposes with evolution of gas and preceding sublimation of crystals with a characteristic shape).

X-ray structure investigation of compound 6 was carried out at 20°C on a Bruker P4 single crystal diffractometer with a graphite monochromator using MoKα radiation. The structure was solved by the direct method and refined with the full-matrix least-squares anisotropic (isotropic for H atoms) approximation using the SHELXL-97 software.[23] The positions of the H atoms were localized geometrically. The crystal was a thin (0.01–0.02 mm) elongated plate. The experiment was carried out up to 2θ 45°, since at larger angles all reflections were of zero intensity. The high *R* value (0.17) has possibly to do with the fact that the crystal was an aggregate, although the twin law was not established. The complete crystallographic information on compound **6** has been deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1999877).

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