Preparation of 1,4,2-Dithiazolium Salts

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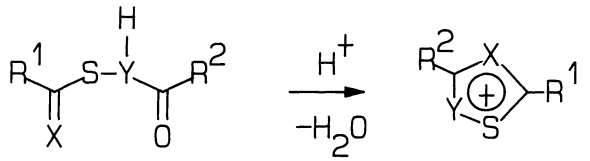
Synopsis. *N*-(Substituted formyl)dialkylamino(thioxo)-methanesulfenamides ($R_2NCSSNHCOR'$ **3**: R=alkyl, R'= alkyl, dialkylamino, alkoxy, and heterocyclic substituent) were treated with a strong acid (HBF_4 or $HClO_4$) in Ac_2O to afford 1,4,2-dithiazolium salts (**7**) and/or 3,5-bis(dialkyliminio)-1,2,4-trithiolanes (**9**). The reactivity is markedly dependent on the nature of substituents (NR_2 and R') and the acid used. For R'=MeO, the sulfenamides reacted successively with NaH and *p*-toluenesulfonyl chloride to give methyl bis(dialkylthiocarbamoylthio)carbamates (**10**). The mechanisms for the formation of **9** and **10** are discussed.

The chemistry of five-membered heteroaromatic cation compounds, which are stabilized by the 6π-electron system satisfying the Hückel's rule, constitutes a well-documented field of research. In particular, 1,3-dithiolium (**5**),[1] 1,3-oxathiolium (**6**),[2] and 1,4,2-dithiazolium systems (**7**)[3] have attracted much attention for their preparation and reactivity to serve as versatile intermediates in organic syntheses. Furthermore, the synthesis of 1,3,4-oxathiazolium salts (**8**) was recently established.[4]



1 ----- X=S, Y=CH ----- 5
2 ----- X=O, Y=CH ----- 6
3 ----- X=S, Y=N ----- 7
4 ----- X=O, Y=N ----- 8

Scheme 1.

There is a general method for preparation of this type of cations by use of precursors (**1**–**4**) of the general formula R^1–C(=X)–S–YH–C(=O)–R^2 where X and Y are given in Scheme 1. In general procedures, the precursors are cyclized by dehydration in strong acidic media to afford the corresponding cations **5**—**8**, respectively.

We have recently developed general methods for preparation of **3** (R^1=dialkylamino and R^2=alkyl, dialkylamino, alkoxy, and hetero-ring).[5] As a continuation of this work, we attemped the conversion of newly synthesized **3** into **7** not only according to the conventional procedure mentioned above but also by means of other methods.

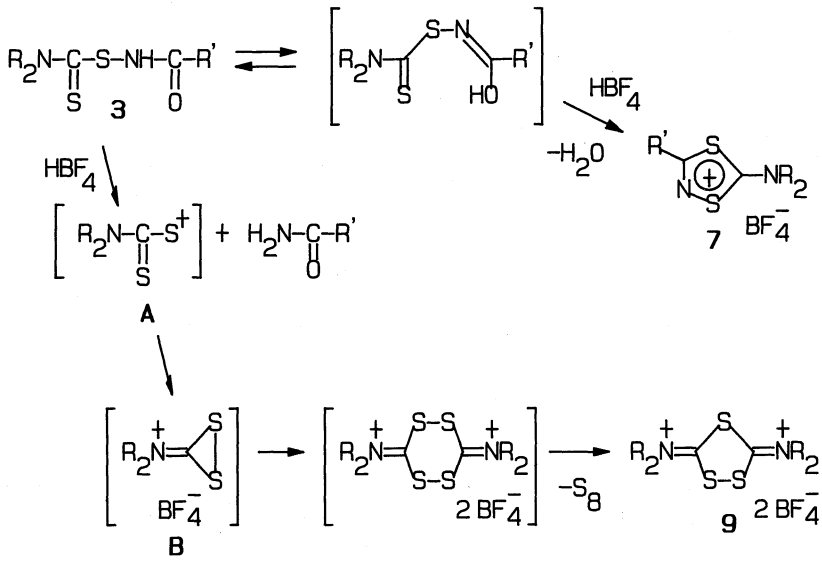
Results and Discussion

First We examined the reaction of **3a**–**d** where R' is an alkyl group. When **3a** and **3b** were treated with HBF_4 in Ac_2O in the same manner as described previously,[3b,g] each reaction gave a white salt as a sole product (Entries 1 and 2 in Table 1). On the basis of their elemental analyses, ^1H NMR spectra (presence of R_2N and R'), IR spectra (presence of BF^-_4), and MS spectra (molecular ion peaks), the products were identified with the targent compounds 1,4,2-dithiazolium salts **7a** and **7b**, respectively. On the contrary, the reaction of **3c** under the same conditions gave a somewhat hygroscopic pale yellow precipitate (Entry 3). On the basis of its elemental analysis and ^1H NMR spectrum which indicated the presence of two equivalent dimethyliminio groups

Table 1. Reaction of Sulfenamides **3** in Strong Acidic Media

Entry	Sulfenamides **3**			Acid	Product yield/%	
	No.	R_2N	R'		**7**	**9**[a]
1	**3a**	Piperidino	*t*-Bu	HBF_4	41	—
2	**3b**	*i*-Pr_2N	Me	HBF_4	46	—
3	**3c**	Me_2N	*t*-Bu	HBF_4	—	96
4	**3d**	Et_2N	Me	HBF_4	—	40
5	**3d**	Et_2N	Me	$HClO_4$	93	—
6	**3e**	Me_2N	2-Thienyl	HBF_4	—	62
7	**3e**	Me_2N	2-Thienyl	$HClO_4$	65	23[b]
8	**3f**	Me_2N	3-Pyridyl	HBF_4	—	54
9	**3f**	Me_2N	3-Pyridyl	$HClO_4$	ca. 90[c]	Low[b]
10	**3g**	Me_2N	Et_2N	HBF_4	—	85
11	**3h**	Me_2N	Et_2N	$HClO_4$	—	91
12	**3i**	Et_2N	MeO	HBF_4	—	42
13	**3j**	Me_2N	MeO	$HClO_4$	—	Quant.

a) Conversion yield. b) The ratios were calculated from the relative area of ^1H NMR signals (dimethylamino groups). c) Pyridinium perchlorate form.



Scheme 2.

(3.68 and 3.73 ppm for $Me_2\overset{+}{N}=$) and the absence of a *t*-Bu group, a diiminium structure, 3,5-bis(dimethyliminio)-1,2,4-trithiolane (**9a**) was proposed. The product was compared with an authentic one prepared by treatment of tetramethylthiuram monosulfide with *m*-chloroperbenzoic acid in HBF_4/Ac_2O, and its structure was confirmed.[6] Treatment of **3d** with HBF_4 gave similarly a 3,5-bis(diethyliminio) derivative **9b** (Entry 4), whereas, on treatment with $HClO_4$, the reaction of **3d** gave 1,4,2-dithiazolium perchlorate **7c** in a good yield (Entry 5).

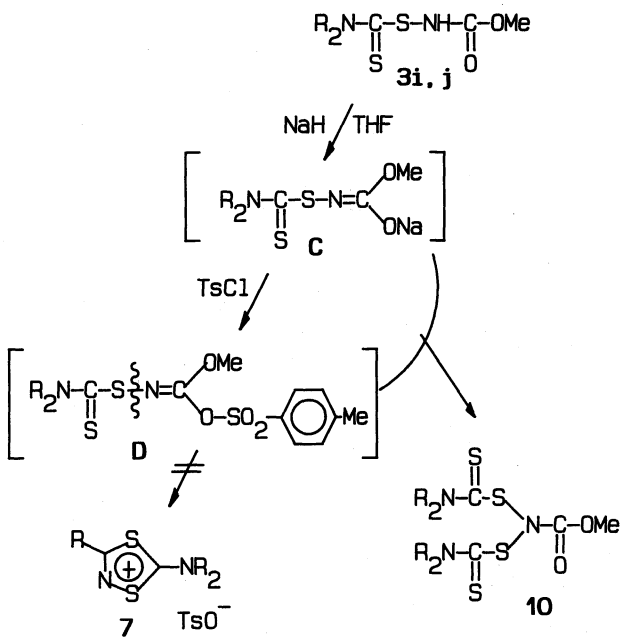
A similar reactivity pattern was observed in the cases of **3e** and **3f** where R′ is a heterocyclic substituent; the sole preparation of **9a** for HBF_4; the preferential formation of **7d** and **7e** for $HClO_4$ (Entries 6–9). In the cases where R′ is a dialkylamino or an alkoxyl group, however, **3g–j** afforded diiminium salts **9** alone on treatment with HBF_4 and $HClO_4$ (Entries 10–13).

The formation of **9** is most likely rationalized by the pathway shown in Scheme 2. Treatment of **3** with acids results in cleavage of the sulfenamide S–N bond to afford dialkylthiocarbamoylthio cations (**A**) as an intermediate together with $R'CONH_2$. The cations **A** are subsequently rearranged to (dialkyliminio)dithiiranes (**B**) followed by dimerization and sulfur extrusion leading to **9**. In Entry 6, 2-thiophenecarboxamide was actually formed in 90% yield. It is known that sulfenamides are generally sensitive to acids resulting in cleavage of the S–N bond.[7] Furthermore, a transient existence of intermediates **A** which arose from dialkyldithiocarbamato complexes of some transition metals by the ligand oxidation and their immediate conversion into **B** and **9** were also reported.[6a,d]

From the above results, it appears that the acid-catalyzed ring-closure reaction of **3** competes with acid-catalyzed cleavage of the S–N bond in **3** and that the selectivity of the reaction is dependent on the nature of substituents (R_2N and R′) and the acid used. However, no reasonable explanation for this can be given at present.

When **3e** was allowed to react in another strong acidic media such as $HBF_4/(CF_3CO)_2O$ and $BF_3{\cdot}Et_2O/CH_2Cl_2$ systems, the reactions gave no 1,4,2-dithiazolium salt **7** but diiminium cation **9a** together with 2-thiophenecarboxamide and a complex mixture, respectively.

We attempted another method without using any acids in order to suppress the cleavage of the S–N bond: after **3** were treated with NaH in dry THF, *p*-toluenesulfonyl chloride (*p*-TsCl) was added to the reaction suspension. In the cases of **3c, e, f,** and **g,** the reactions gave complex mixtures including the corresponding tetraalkylthiuram disulfides, whereas in the cases of **3i** and **j**, the sole formation of bis(dialkylthiocarbamoylthio)carbamic acid methyl esters (**10a** and **10b**) was observed in 91% and



Scheme 3.

almost quantitative conversion yields, respectively. A speculative mechanism for the formation of **10** is shown in Scheme 3. Although it was anticipated that a finally-formed intermediate (**D**) would be cyclized to afford **7** as a tosylate, the actural reaction course was different. It seems that conversion of **C** into **D** is a rate-determining step and that the in situ generated **D** which is equivalent to R_2NCSS^+ as a synthon, reacts exclusively with unaltered **C** to afford **10**. Even inverse dropwise addition of the reaction suspension of **C** to *p*-TsCl in THF had no influence on the yield of **10** (91%→88%). This finding supports the proposed mechanism including the rate-determining step (**C**→**D**).

Experimental

All melting points were uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Hitachi R-40 and a JEOL FX-90A spectrometer using TMS as a internal standard. Mass spectra were taken on a Hewlett Packard 5995A spectrometer by electron impact ionizing technique at 70 eV. IR spectra were measured on a JASCO A-302 spectrometer using KBr disks.

Sulfenamides **3b** and **3d** were readily prepared from the reaction of the corresponding *S*-(dialkylthiocarbamoyl)sulfenamides with acetic anhydride as solvent. The rest of the sulfenamides were prepared from the corresponding amide-type compounds ($R'CONH_2$) according to previous procedures.[5]

Reaction of Sulfenamides 3 in Strong Acidic Media. To a cooled acetic anhydride solution (5 ml) of 40% tetrafluoroboric acid (0.5 ml) or 70% perchloric acid (0.5 ml), sulfenamides **3** (2 mmol) were added with stirring. The reaction mixture was stirred for ca. 1 h at room temperature, during which time the products might precipitate. An excess of ether was poured into the cooled mixture. The precipitate thus formed was collected by filtration and air-dried, which was recrystallized from an appropriate solvent. The yields of **7** and **9** are presented in Table 1. Identification of **9** was performed by direct comparison with authentic ones prepared by treatment of tetramethylthiuram monosulfide or tetraethylthiuram disulfide (including sulfur-extrusion step) with mCPBA in HBF_4/Ac_2O or $HClO_4/Ac_2O$.[6]

3-(*t*-Butyl)-5-piperidino-1,4,2-dithiazolium Tetrafluoroborate 7a: Mp 153.0—154.0 °C (MeCN–ether). ^1H NMR ($CDCl_3$) δ=1.46 (9H, s), 1.7—2.1 (6H, m), 3.7–3.9 (2H, m), 3.9—4.1 (2H, m). IR ν 1579, 1000—1200(BF_4) cm^{-1}. MS *m/z* (rel intensity) 243(M^+, 34), 160 (32), 146 (100), 128 (93), 83 (86). Found: C, 39.75; H, 5.86; N, 8.03%. Calcd for $C_{11}H_{19}N_2S_2BF_4$: C, 40.01; H, 5.80; N, 8.48%.

5-Diisopropylamino-3-methyl-1,4,2-dithiazolium Tetrafluoroborate 7b: Mp 126.0—127.5 °C (CH_2Cl_2–ether). ^1H NMR ($CDCl_3$) δ=1.54 (12H, d, *J*=6.3 Hz), 2.79 (3H, s), 4.0—4.6 (2H, m). IR ν 1550, 1000—1200 (BF_4) cm^{-1}. MS *m/z* (rel intensity) 217 (M^+, 5), 176 (36), 100 (31), 58 (100). Found: C, 35.37; H, 5.89; N, 8.93%. Calcd for $C_9H_{17}N_2S_2BF_4$: C, 35.54; H, 5.63; N, 9.21%.

5-Diethylamino-3-methyl-1,4,2-dithiazolium Perchlorate 7c: Mp 88.5—89.5 °C (MeCN–ether). ^1H NMR ($CDCl_3$) δ=1.48 (6H, t, *J*=7.2 Hz), 2.77 (3H, s), 3.83 (2H, q, *J*=7.2 Hz), 3.93 (2H, q, *J*=7.2 Hz). IR ν 1587, 1565, 1000—1200 (ClO_4) cm^{-1}. MS *m/z* (rel intensity) 189 (M^+, 36), 148 (23), 116 (43). Found: C, 28.86; H, 4.45; N, 9.72; S, 22.34%. Calcd for $C_7H_{13}N_2S_2ClO_4$: C, 29.11; H, 4.54; N, 9.70; S, 22.21%.

5-Dimethylamino-3-(2-thienyl)-1,4,2-dithiazolium Perchlorate 7d: Mp (decomp) 216.0—218.0 °C (AcOH–H_2O). ^1H NMR (CD_3CN) δ=3.47 (3H, s), 3.60 (3H, s), 7.2—7.4 (1H, br.t), 7.7—7.8 (1H, br.dd), 7.85—7.95(1H, br.dd). IR ν 1602, 1541, 1494, 1000—1200 (ClO_4) cm^{-1}. Found: C, 28.64; H, 2.87; N, 8.43%. Calcd for $C_8H_9N_2S_3ClO_4$: C, 29.22; H, 2.76; N, 8.52%.

5-Dimethylamino-3-(3-pyridinio)-1,4,2-dithiazolium Diperchlorate 7e: Mp 272.0—275.0 °C (AcOH–H_2O). ^1H NMR (CD_3CN) δ=3.51 (3H, s), 3.68 (3H, s), 7.2—7.4 (1H, m), 7.8—8.3 (3H, m). IR ν 1618, 1533, 1000—1200 (ClO_4) cm^{-1}. Found: C, 25.05; H, 2.89; N, 9.82; S, 15.18%. Calcd for $C_9H_{11}N_3S_2$ (ClO_4)$_2$: C, 25.48; H, 2.61; N, 9.90; S, 15.12%.

Reaction of Sulfenamides 3 with NaH/TsCl. Sodium hydride (ca. 60% in oil)(40 mg; 1 mmol) was added to a dry THF solution (6 ml) of sulfenamides **3** (1 mmol). The reaction mixture was stirred for ca. 15 min at room temperature. After the evolution of hydrogen ceased, *p*-toluenesulfonyl chloride (190 mg; 1 mmol) was added to the cooled reaction suspension, which was stirred for 30 min at room temperature. The crude product was extracted with dichloromethane after addition of an aqueous sodium hydrogencarbonate. After the solvent was removed in vacuo, the residue was purified by preparative TLC on silica gel and recrystallized from CH_2Cl_2–pentane.

Methyl Bis(diethylthiocarbamoylthio)carbamate 10a: Mp 130.0—131.0 °C. ^1H NMR ($CDCl_3$) δ=1.28 (6H, t, *J*=7.2 Hz), 3.3—4.2 (4H, br.), 3.79 (3H, s). ^{13}C NMR ($CDCl_3$) δ=11.72, 44—52 (br.), 55.30, 155.84, 194.01. IR ν 1743, 1585, 1418 cm^{-1}. MS *m/z* (rel intensity) 369 (M^+, 0.7), 116 (100), 88 (80). Found: C, 38.90; H, 6.07; N, 11.87; S, 34.58%. Calcd for $C_{12}H_{23}N_3S_4O_2$: C, 39.00; H, 6.27; N, 11.37; S, 34.70%.

Methyl Bis(dimethylthiocarbamoylthio)carbamate 10b: Mp 160.5—161.0 °C. ^1H NMR ($CDCl_3$) δ=3.40 (6H, br.s), 3.81 (3H, s).^{13}C NMR ($CDCl_3$) δ=39.9 (br.), 45.0 (br.), 55.57, 155.84, 195.20. IR ν 1741, 1508, 1385, 1238 cm^{-1}. MS *m/z* (rel intensity) 240($(Me_2NCSS)_2^+$,4), 120 (10), 88 (100). Found: C, 30.62; H, 4.49; N, 13.09; S, 40.77%. Calcd for $C_8H_{15}N_3S_4O_2$: C, 30.65; H, 4.82; N, 13.40; S, 40.91%.

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