

Preparation and Thermal Degradation of α,ω -Alkylene
Bis[5-(1,2,3,4-thiazotriazolyl)] Sulfides

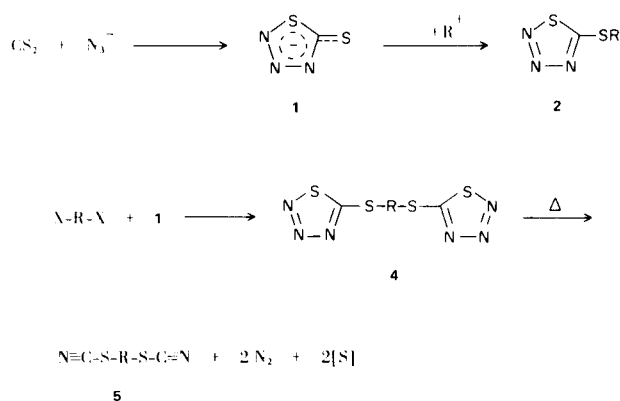
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Syntheses of some extremely shock sensitive α,ω -alkylene bis[5-(1,2,3,4-thiazotriazolyl)] sulfides *via* reaction of sodium 1,2,3,4-thiazotriazoline thionate (**1**) and α,ω -dihaloalkanes are described. Dichloromaleic imide reacted analogously with **1** to give 3,4-bis(5-(1,2,3,4-thiazotriazolyl)thio)maleic imide. The compounds decompose thermally in solution with formation of α,ω -alkylene bis(thiocyanates), nitrogen and sulfur. The infrared spectra are discussed.

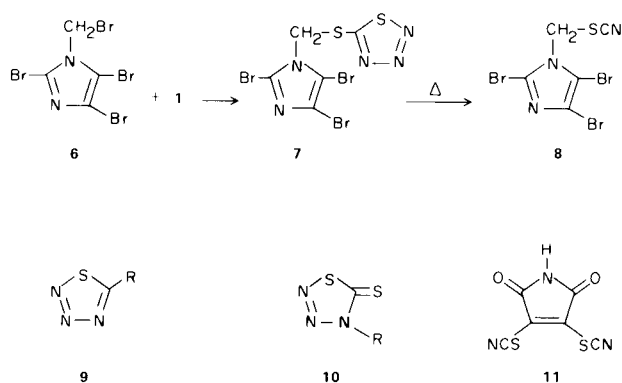
The recognition that the class of carbon disulfide-azide ion condensation products, once regarded as azidodithiocarbonates (**3**) actually possess the 1,2,3,4-thiazotriazole ring skeleton (4,5) has stimulated interest in synthetic approaches to the latter framework (**6**). In accord with this view, treatment of the reaction product of carbon disulfide with azide ion, namely 1,2,3,4-thiazotriazoline thionate (**1**), with an alkylating reagent was found to yield only 5-alkylthio-1,2,3,4-thiazotriazoles (**7**) (**2**). In extending this general reaction to **1** and bifunctional dihalogeno compounds (**3**), we hoped to isolate and further degrade the α,ω -alkylene bis[5-(1,2,3,4-thiazotriazolyl)] sulfides (**4**) with a view to obtaining pure α,ω -alkylene bis(thiocyanates) (**5**) and not mixtures of thiocyanate and isothiocyanate (**8**).



When aqueous solutions of **1** (**7**) were allowed to react with α,ω -dihalogeno alkanes (**3**; R = (CH₂)_n,

n = 1-4) at ambient temperature over a period of two to eight hours, **4** could be isolated in crystalline form by filtration in moderate to high yield. 1,4-Bis(iodomethyl)cyclohexane (**9**) (**3e**) and dichloromaleic imide (**3f**) reacted analogously to give the corresponding disubstituted products, **4e** and **4f**, respectively (Table I). *N*-Bromomethyl-2,4,5-tribromoimidazole (**6**) gave only a monosubstituted product, namely **7**. Compounds **4** and **7** are thermally stable, not decomposing when heated close to their melting point. However, compounds **4** are extremely sensitive to shock and decompose violently on impact (**10**). They were characterized by infrared spectral analysis (Table II) and controlled thermal degradation (see below).

In conformity with the 1,2,3,4-thiazotriazole structure, compounds **4** and **7** contain neither covalent nor ionic azide groups as the azide band near 2100 cm⁻¹ is absent from their spectra. However, the most important observation arising from an inspection of the infrared spectral data of **4** and **7** is the complete transparency in the 2800-1500 cm⁻¹ region (**11**). Jensen, *et al.* (**12**) have reported a medium strong infrared band near 1575 cm⁻¹ in compounds of general structure **9** (R = aryl, NHR¹, NR¹R²) and assign this band to the interaction between C=N, N=N, C-S and N-S stretching vibrations of the heteroaromatic ring. Lieber, *et al.* (**7**) have found characteristic frequencies of the 1,2,3,4-thiazotriazole ring (**2**; R = aralkyl, methyl, phenacyl, CN, and **10**; R = aralkyl, benzoyl) in the regions 1610-1560(w), 1320-1280(v), 1240-1190(v) and 1090-1000(v) cm⁻¹. While it is true that bands in the latter three regions are observed in the infrared spectra of **4** and **7**, the uniform absence of the 1610-1560 cm⁻¹ band indicates that it may not be characteristic of the 1,2,3,4-thiazotriazole ring.



Compounds **4a-d** and **7** were converted in high yield to the corresponding thiocyanato derivatives, **5** and **8**, respectively, in hot benzene (Table III). Thermal decomposition of the maleic imide derivative (**4f**) in hot benzene proceeded normally in that evolution of nitrogen occurred. However, the bis(thiocyanato) compound (**11**) was not isolated as it polymerized forming a solid containing sulfur. The instability of **11** is not unexpected in view of its

similarity to thiocyanogen, $(\text{SCN})_2$, of which it is a vinylog and which is known to polymerize readily (13).

Evidence for the structure of **5** and **8** as thiocyanato compounds was unambiguous from their infrared spectra which showed a characteristic sharp nitrile frequency near 2150 cm^{-1} . With the exception of **4b** which showed a small shoulder at 2100 cm^{-1} , all other analogs had no absorption in the isothiocyanate region $2100\text{-}2020 \text{ cm}^{-1}$. Additional prominent infrared peaks are listed in Table III.

EXPERIMENTAL

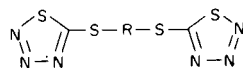
Infrared spectra (Table II and Table III) were recorded on a Perkin Elmer Model 21 Spectrometer in the form of potassium bromide discs. All melting and boiling points are uncorrected.

Methylene Bis[5-(1,2,3,4-thiazololyl)] Sulfide (**4a**).

To a solution of 0.36 mole of the sodium salt of 1,2,3,4-thiazololone (7) (**1**) in 100 ml. of water was added with stirring a solution of 48.3 g. (0.18 mole) of methylene iodide (**3a**) in 400 ml. of acetone. This solution was stirred for 3 hours and left standing overnight at ambient temperature. Water was added and the light yellow precipitate was removed by filtration, washed with 400 ml. of warm (35°) acetone-methanol (1:1) and dried to give 40.0 g. (89%) of **4a**. Compounds **4b**, **4c**,

TABLE I

α,ω -Alkylene Bis(5-(1,2,3,4-thiazololyl) Sulfides



Compound	R	Starting Material No.	X-R-X (X given)	Yield, %	M.p. °C (a)	Formula	C Calcd. Found	H Calcd. Found	N Calcd. Found
4a	$-(\text{CH}_2)-$	3a	I	89.0	99 (b)	$\text{C}_3\text{H}_2\text{N}_6\text{S}_4$	14.4 14.0	0.8 0.8	33.6 33.8
4b	$-(\text{CH}_2)_2-$	3b	Br	28.3	93	$\text{C}_4\text{H}_4\text{N}_6\text{S}_4$	18.2 17.9	1.5 1.4	31.8 31.4
4c	$-(\text{CH}_2)_3-$	3c	I	22.6	85	$\text{C}_5\text{H}_6\text{N}_6\text{S}_4$	21.6 21.7	2.2 2.3	30.1 30.3
4d	$-(\text{CH}_2)_4-$	3d	Br	20.9	75	$\text{C}_6\text{H}_8\text{N}_6\text{S}_4$	24.6 24.3	2.7 2.8	28.8 28.5
4e		3e	I	41.0	92	$\text{C}_{10}\text{H}_{14}\text{N}_6\text{S}_4$	34.7 34.7	4.0 4.4	24.3 24.5
4f		3f	Cl	58.0	91	$\text{C}_6\text{HN}_7\text{O}_2\text{S}_4$	21.7 21.8	0.3 <0.5	29.6 29.9

(a) With decomposition. (b) Nitrogen is evolved at 80° without melting of the sample.

TABLE II
Important Characteristic Vibrations of 1,2,3,4-Thiazolones (cm^{-1})

Compound	3000-2835 (a) (m)	1315-1300 (b) (vs)	1232-1215 (vs)	1080-1060 (s, broad)	1000-965 (w)	905-890 (m)
4a	2984, 2930	1300	1225	1060	980	890
4b	3000, 2900	1315	1230	1065	995	895
4c	3000-2900	1310	1232	1080	1000	900
4d	2945, 2920	1312	1225	1070	1000	900
4e	2900, 2835	1300	1230	1066	1000	890
4f	-----	1315	1225	1075	985	905
7	2995, 2945	1315	1215	1075	965	900

(a) CH stretching vibration. (b) All bands have a shoulder at higher wave length (+0.1 μ).

TABLE III
 α,ω -Alkylene Bis(thiocyanates), $\text{N}\equiv\text{C}\cdot\text{S}\cdot\text{R}\cdot\text{S}\cdot\text{C}\equiv\text{N}$

Compound (a)	R	Yield, %	M.p. °C or B.p. °C (mmHg)	Lit., M.p. or B.p.	Band Positions (cm^{-1})				
					3000-2900 (b) (m)	2160-2140 (c) (s)	1410-1070 (s)	(s)	(m)
5a	-CH ₂ -	88.5	101-102	102 (14)	3011 2950	2156	1370	1200	1150
5b	-(CH ₂) ₂ -	72.4	89-90	90 (15)	2993 2950	2142	1410	1206	1130
5c	-(CH ₂) ₃ -	74.0	22 110 (0.01)	23 (16)	3000 2900	2150	1410	1205	1080
5d	-(CH ₂) ₄ -	58.0	120 (0.01)	193-195 (13)(17)	2945 2920	2147	1400	1205	1070

(a) Satisfactory analytical data have been obtained on every compound. (b) CH stretching vibration. (c) Nitrile band.

4d, and 4e were prepared analogously. Analytical and spectral data are recorded in Table I.

Bis[5-(1,2,3,4-thiazolyl)thio]maleic Imide (4f).

A solution of 0.76 mole of the sodium salt of 1 in 50 ml. of water was added dropwise within 15 minutes to a cold (-25 to -15°) solution of 14.6 g. (88 mmoles) of dichloromaleic imide (18) (3f) in 300 ml. of acetone with stirring causing a yellow solid to precipitate out. This procedure was chosen because the inverse addition is extremely exothermic and could not be controlled by external cooling. After the addition was completed, ice water, 500 ml., was added, the solid was removed by filtration, washed well at -5 to 0° with cold acetone or methanol and dried in a desiccator over anhydrous calcium chloride, yield 23.0 g. (58%), ir absorption, 3265 (NH), 1780 and 1720 (C=O) and 1575 cm^{-1} (C-C). Analytical and additional spectral data are listed in Table I and Table II.

2,4,5-Tribromo-1-[5-(1,2,3,4-thiazolyl)]thiomethyl Imidazole (7).

To a solution of 61.5 mmoles of 1 (sodium salt) in 20 ml. of water was added with stirring a solution of 23.8 g. (0.06 mole)

of *N*-bromomethyl-2,4,5-tribromoimidazole (19) (6) in 70 ml. of acetone. After standing overnight at ambient temperature, 100 ml. of ice was added causing a white solid to precipitate. This solid was recrystallized from aqueous methanol with the aid of charcoal to give 10.0 g. (38%) of 7, white crystalline solid, m.p. 80.5° dec., not sensitive to shock.

Anal. Calcd. for $\text{C}_5\text{H}_2\text{Br}_3\text{N}_5\text{S}_2$: C, 13.8; H, 0.5; N, 16.0. Found: C, 13.7; H, 0.6; N, 15.8.

Thermolysis of Thiazolones 4a-d.

General Procedure.

A mixture of 4 (0.1 mole) in 500 ml. of benzene was gradually heated with stirring until nitrogen began to evolve. The rate of thermolysis was followed volumetrically by measuring the amount of nitrogen gas evolved. After completion of the reaction, the reaction mixture was filtered, concentrated and purified by distillation (to give 5c and 5d). In the case of 4a and 4b, the crude reaction mixture was treated with 0.2 moles of trimethyl phosphite in order to dissolve sulfur. The clear reaction mixture was concentrated and recrystallized from methanol (to give 5c and 5d). Physical and spectral data are listed in Table III.

2,4,5-Tribromo-1-thiocyanomethyl Imidazole (**8**).

A mixture of 8.72 g. (0.02 mole) of **7** in 250 ml. of benzene was heated with stirring at 75° until nitrogen evolution ceased (2.5 hours). The reaction mixture was filtered, concentrated and recrystallized from ethanol (charcoal) to give 6.5 g. (81%) of light yellow crystalline **8** melting at 116°.

Anal. Calcd. for C₅H₂Br₃N₃S: C, 16.0; H, 0.5; N, 11.2. Found: C, 16.3; H, 0.5; N, 11.1.

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- (8) In connection with another problem related to the reaction of organic thiocyanates with trialkyl phosphites, we wished to have at our disposal a series of pure α,ω -alkylene bis(thiocyanates), **5**. Investigation by infrared spectroscopy of the reaction products obtained from potassium thiocyanate with methylene iodide (**14**), ethylene dibromide (**15**), 1,3-dibromopropane (**16**) and 1,4-dibromobutane (**17**) revealed mixtures of thiocyanate and isothiocyanate, presumably of the type S=C=N(CH₂)_n-S-C≡N.
- (9) The stereochemistry of **3e** was not determined.
- (10) In a preliminary communication on this subject: K. Pilgram and F. Korte, *Angew. Chem.*, **77**, 348 (1965); *Angew. Chem. Int. Ed. Engl.*, **4**, 357 (1965), we described the extreme shock sensitivity of this class of compounds.
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