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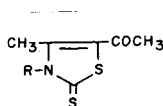
St. Louis, Missouri 63166

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The reaction of various potassium or ammonium salts $[\text{RNHC}(=\text{S})\text{SM}]$, $\text{M} = \text{K}$ or NH_4 ; $\text{R} = \text{N}(\text{CH}_3)_2$, morpholino, pyrrolidino, piperidino, and hexahydro-1-(1*H*)-azepinyl] with 2-chlorocyclohexanone in alcohol at 25-30° afforded the title compounds **1** and **3-6**. The treatment of these compounds with a catalytic amount of *p*-toluenesulfonic acid in refluxing benzene furnished the dehydrated products **2** and **7-10**. The reaction of potassium dithiocarbamate with 2-chlorocyclohexanone or 3-chloro-3,4-pentanedione in refluxing ethanol afforded **11**, a six membered heterocycle and **12**, a five membered heterocycle, respectively. Possible mechanisms and supporting nmr, ir, uv mass spectral data are discussed.

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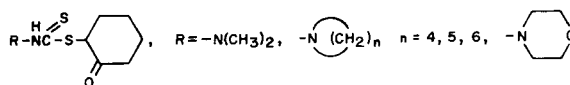
In a previous communication [2] we reported that the reaction of potassium substitutedaminodithiocarbamates $\text{RNHC}(=\text{S})\text{SK}$, $\text{R} = \text{N}(\text{CH}_3)_2$, morpholino, pyrrolidino, piperidino, and hexahydro-1-(1*H*)-azepinyl] with 3-chloro-2,4-pentanedione in ethanol at 25-30° afforded the 1-acetylacetyl substitutedaminodithiocarbamates $\text{RNHC}(=\text{S})\text{SCH}(\text{COCH}_3)_2$. Under refluxing temperatures, the same reactions furnished 3-substituted-4-methyl-5-acetyl-4-thiazoline-2-thiones.



Thus, it appeared expedient to continue our investigation of the above salts and potassium or ammonium salts of dithiocarbamates with 2-chlorocyclohexanone.

The reaction of 2-chlorocyclohexanone with the appropriate ammonium or potassium substitutedaminodithiocarbamates in alcohol at 25-30° afforded 3a,4,5,6,7a-hexahydro-3a-hydroxy-3-(dimethylamino)-2-benzothiazolinethione (**1**), 3a,4,5,6,7a-hexahydro-3a-hydroxy-3-pyrrolidinyl-2-benzothiazolinethione (**3**), 3a,4,5,6,7a-hexahydro-3a-hydroxy-3-morpholino-2-benzothiazolinethione (**4**), 3a,4,5,6,7a-hexahydro-3a-hydroxy-3-piperidino-2-benzothiazolinethione (**5**) or 3a,4,5,6,7a-hexahydro-3a-hydroxy-3-(hexahydro-1*H*-1-azepinyl)-2-benzothiazolinethione (**6**).

Increasing the temperature from 25 to 80° in the reaction between potassium dimethylaminodithiocarbamate and 2-chlorocyclohexanone furnished the dehydrated product, 4,5,6,7-tetrahydro-3-(dimethylamino)-2-benzothiazolinethione (**2**). However, the 80° reaction temperature in the reaction of potassium piperidinodithiocarbamate and 2-chlorocyclohexanone did not give the expected dehydrated product (**9**) but instead furnished **5**. The above reactions are depicted in Figure 1. However, based on elemental analysis and molecular weight determinations, the following ester structures of substituted aminodithiocarbamic acids had to be considered:

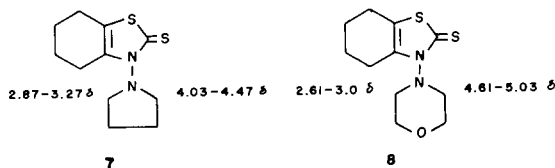


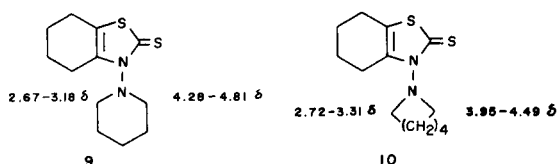
The ir spectra obviated the above ester structures as no $\text{C}=\text{O}$ or NH adsorption bands were observed, while OH adsorption bands at $3500\text{-}3100\text{ cm}^{-1}$ were found. Moreover, the nmr spectra exhibited OH protons, which exchanged with deuterium oxide and the absence of the NH protons. Furthermore, the mass spectrum for **4** is in complete agreement with the proposed structure. The mass fragmentation pattern is shown in Scheme I. In conclusion, the ir, nmr, and mass spectral data confirm the proposed structures **1**, **3**, **4**, **5**, and **6** and ruled out the open chain ester structures.

The proposed mechanism for the formation of **1**, **3**, **4**, **5**, and **6** is shown in Scheme II.

The treatment of **3**, **4**, **5**, and **6** with a catalytic amount of *p*-toluenesulfonic acid in refluxing benzene for 3 hours effected the desired dehydration reaction to afford the corresponding 4,5,6,7-tetrahydro-2-benzothiazolinethiones, **7**, **8**, **9**, and **10** shown in Table I and Figure 1. The elemental analysis and nmr spectral data confirmed these proposed structures for **2**, **7**, **8**, **9**, and **10**. Moreover, the electron mass spectrum for **8** afforded the molecular weight in the form of M^+ at m/e 256. The mass fragmentation (Scheme III) is consistent for structure **8**. The dehydration of **1**, **3**, **4**, **5**, and **6** to give **2**, **7**, **8**, **9**, and **10**, respectively, constitutes additional proof of structure for the former compounds.

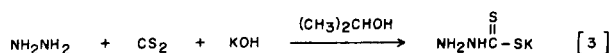
In the nmr spectra of compounds **7-10** the protons adjacent to the nitrogen and in close proximity to the cyclohexene and thiocarbonyl moieties are of particular interest.



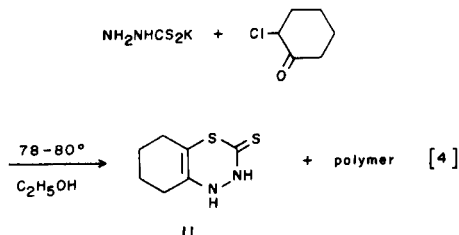


The large shift of the downfield protons is attributed to the large deshielding effect of the thiocarbonyl group.

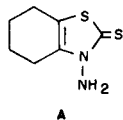
Potassium dithiocarbazate was prepared by the method described by Busch and Starke [3].



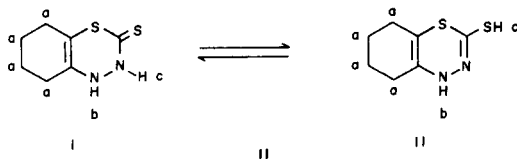
However, this salt is stable for only 3 to 4 hours after isolation. The freshly prepared potassium dithiocarbazate was reacted with 2-chlorocyclohexanone in ethanol at reflux to give 5,6,7,8-tetrahydro-1H-4,1,2-benzothiadiazin-3(2H)-thione (**II**), plus an insoluble polymeric material.



Attempts to isolate **II** from the polymer by treatment with dilute sodium hydroxide/hydrochloric acid proved partially successful. Under these conditions, a small portion of **II** could be recovered. However, the sensitivity of crude **II** to alkali or acid excluded this treatment and the separation could be better effected by a recrystallization of the crude mixture from ethyl acetate to give a 30% yield of **II**, mp 136-137°. The elemental analysis and molecular weight data for **II** afforded an empirical formula, $\text{C}_7\text{H}_{10}\text{N}_2\text{S}_2$ and alternate structure **A**, had to be considered.



However, structure **A** was ruled out by nmr, ir, uv and mass spectral data:

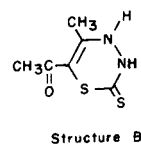


nmr: δ 1.00-3.02 (m, 8, a), 3.48-4.02 (m, 1, b), 10.68 (broad s, 1, c). The large downfield shift of one of the NH protons

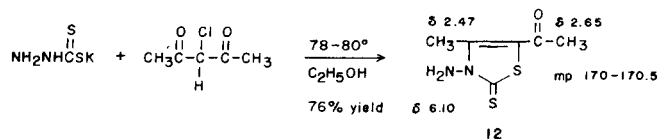
(10.68 ppm) is the key to ruling out structure **A** in favor of the proposed structure **II**. It not only indicates non-equivalence of the two NH protons but also suggests one is acidic which could not be the case if the $-\text{NH}_2$ were present as in **A**. However, this evidence would be expected in the indicated thioamide tautomerism shown above. The existence of this tautomerism was confirmed for **II** as a sample could be titrated potentiometrically in isopropyl alcohol with tetrabutylammonium hydroxide to give a neutral equivalent of 182, theory -186. In addition, recrystallized **II**, mp 136-137°, was soluble in dilute sodium hydroxide and reprecipitated upon the addition of dilute hydrochloric acid. The $\mu\nu$ spectral data are in agreement with the proposed structure for **II**. $A_s = 81.7$ at $323 \text{ m}\mu$ in methanol; $A_s = 44.6$ at $325 \text{ m}\mu$ in methanol + sodium hydroxide. From the ir spectral study, it can be concluded that **II** in the solid state exists mainly in the thioamide form I. This conclusion was based on the absence of the $-\text{SH}$ absorption band at $2400\text{-}2575 \text{ cm}^{-1}$ and the presence of the following absorption bands (potassium bromide): 3216 (NH of a secondary NH), 1301 ($>\text{N}-\text{C}(=\text{S})-\text{S}$ mode) and 1086 ($\text{C}=\text{S}$) cm^{-1} .

The electron impact mass spectrum for **II** furnished the molecular weight data in the form of M^+ at m/e 186. The mass fragmentation pattern (Scheme IV) is in agreement with the proposed structure of **II**. The proposed mechanism for the formation of **II** is depicted in Scheme V.

It was anticipated that since the reaction of potassium dithiocarbazate with 2-chlorocyclohexanone furnished the six-membered heterocycle, **II**, replacing the above electrophile with 3-chloro-2,4-pentanedione [4] should under the same conditions result in formation of structure **B**.



However, this postulate was not substantiated and the product isolated in this reaction was 5-acetyl-3-amino-4-methyl-4-thiazolin-2-thione (**12**).



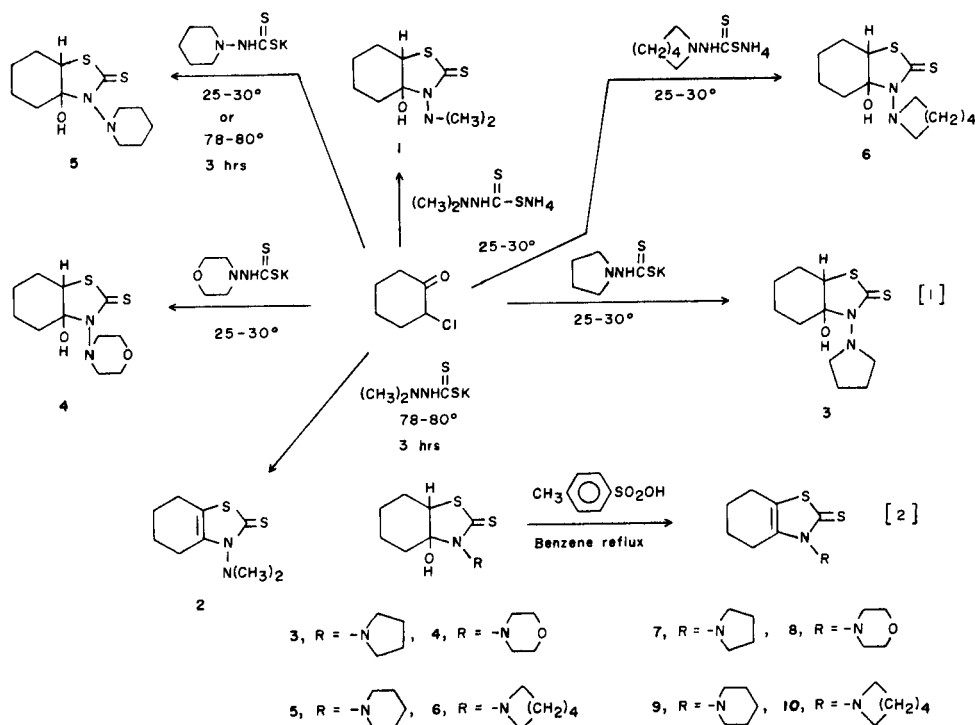
In the above reaction, no evidence for the formation of **B** or polymers was detected. The nmr, $\mu\nu$, ir and mass spectral data ruled out structure **B** and confirmed the proposed structure **12**. If structure **B** were the correct structure, two non-equivalent N-H protons should be observed in the nmr spectrum. This was not the case and the two equivalent NH_2 protons were observed at δ 6.10.

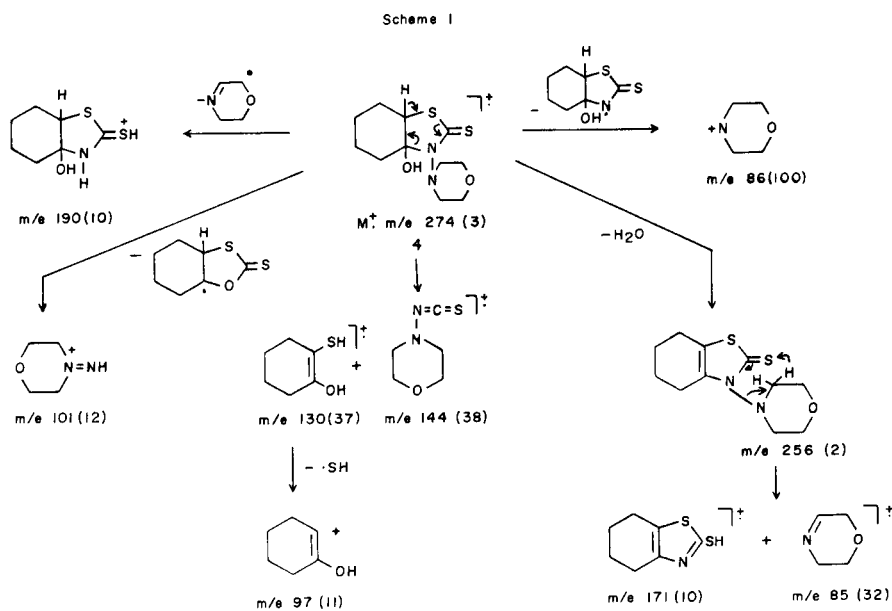
Table 1

No.	Mp °C	% Yield	NMR δ , ppm CDCl ₃ -(Me ₄ Si)	Empirical Formula	%C		%H		%N		%S	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
7 [6]	184-185 [1]	56	1.57-2.30 (m, 8, a) 2.30-2.67 (m, 4, b) 2.87-3.27 (m, 2, c) 4.03-4.47 (m, 2, d)	C ₁₁ H ₁₆ N ₂ S ₂	54.96	54.90	6.71	6.71	11.65	11.52	26.68	26.52
8 [4,6]	184-185 [2]	97	1.50-2.10 (m, 4, a) 2.09-2.63 (m, 4, b) 2.61-3.00 (m, 2, c) 3.28-4.08 (m, 4, d) 4.61-5.03 (m, 3, e)	C ₁₁ H ₁₆ N ₂ OS ₂	56.53	56.31	6.29	6.12	10.93	10.78	25.01	24.91
9 [6]	151 [3]	97	1.08-2.13 (m, 10, a) 2.14-2.66 (m, 4, b) 2.68-3.18 (m, 2, c) 4.28-4.81 (m, 2, d)	C ₁₂ H ₁₈ N ₂ S ₂ [5]	56.65	56.83	7.13	7.30	11.01	11.01	25.21	25.13
10 [6]	118-119 [1]	87	1.09-2.01 (m, 12, a) 2.29-2.70 (m, 4, b) 2.72-3.31 (m, 2, c) 3.95-4.49 (m, 2, d)	C ₁₃ H ₂₀ N ₂ S ₂ [6]	58.16	58.14	7.51	7.53	10.44	10.44	23.89	23.79

[1] Recrystallization from heptane-ethanol. [2] Recrystallization from ethyl acetate. [3] Recrystallization from heptane-2-propanol (1:1). [4] Electron mass spectrum m/e (relative intensity) M^+ : 256 (18), 171 (100), 143 (18), 138 (17), 126 (3), 112 (5), 111 (5), 95 (6), 86 (30), and 85 (32). [5] Calcd. MW 254.4. Found: 260 (DMF). [6] Calcd. MW 268.4. Found: 268 (DMF). [7] The methylene protons adjacent to the C=S group (d in 7, 9, 10 and e in 8) were found further downfield due to the deshielding effect of the thiocarbonyl moiety.

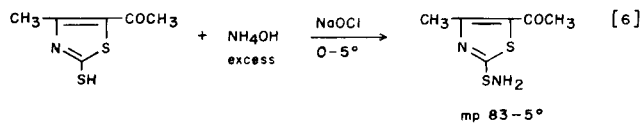
Figure 1





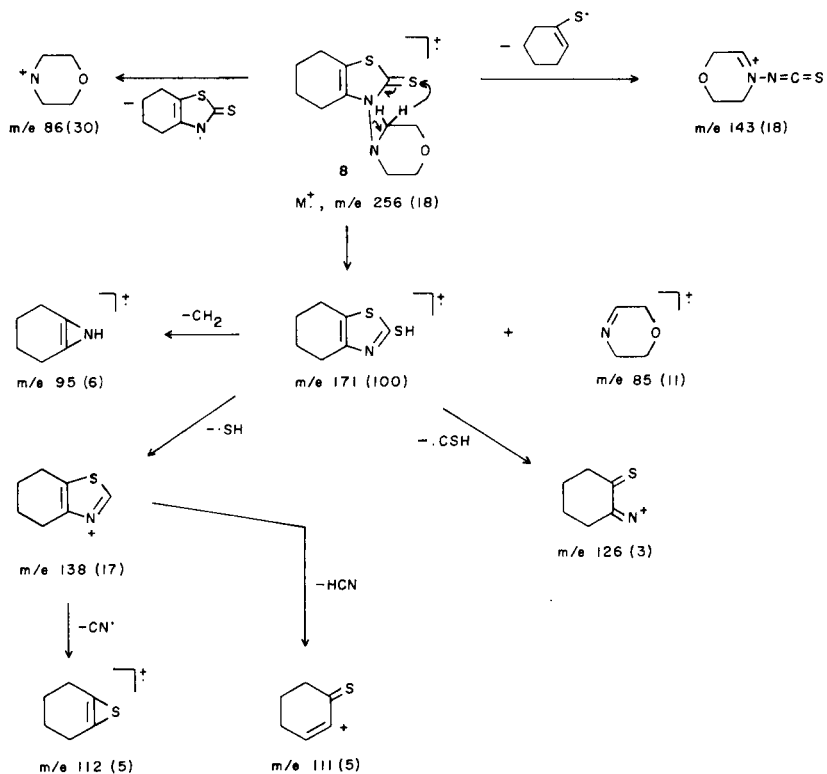
The $\mu\nu$ spectral data also supported the proposed structure **12**. The spectrum in methanol shows $A_{\nu} = 93.4$ at $353 \mu\mu$ (which does not change with sodium hydroxide). In addition no evidence of acidic protons was found upon attempted titration of a sample of **12** with 0.1N tetrabutyl ammonium hydroxide. Moreover, the ir spectral data were in complete agreement for the proposed structure **12**. This conclusion was based on the observance of the following absorption bands: (potassium bromide), 3227 and 3144 (H-bonded NH of NH₂), 1676 (C=O), 1606 (NH₂ deform), 1276 and 1234 (>N-C(=S)-S-) and 1174 (C=S) cm^{-1} . The electron impact mass spectrum for **12** furnished the molecular weight in the form of M⁺: at m/e 188. Furthermore,

the fragmentation pathway for **12** (Scheme VI) is consistent with the proposed structure **12**. A proposed mechanism for the formation of **12** is shown in Scheme VII. An isomer of **12** was reported [5] as illustrated by the following reaction:

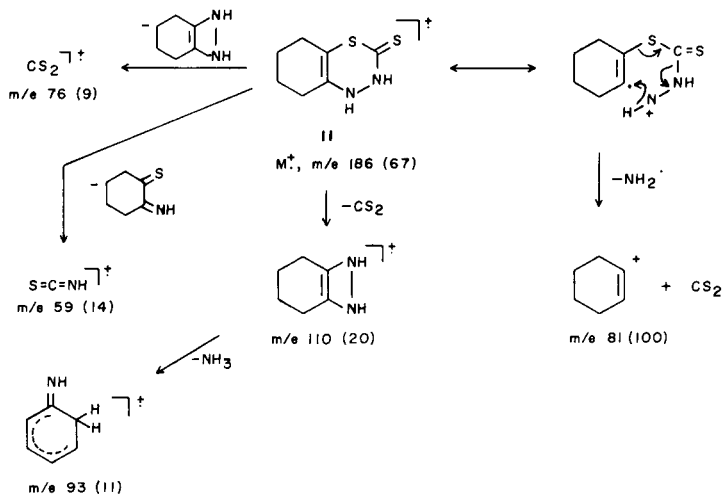


These data on the isomeric structure furnished additional support for the validity of proposed structure **12**.

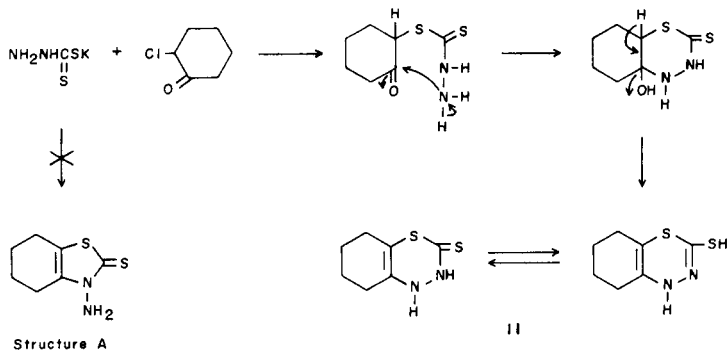
Scheme III

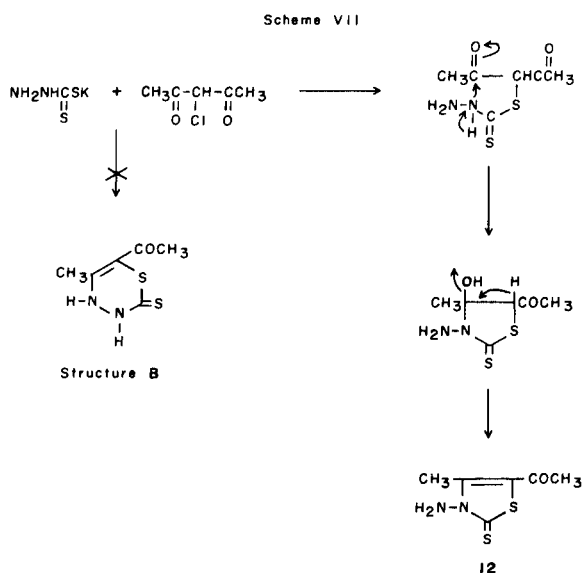
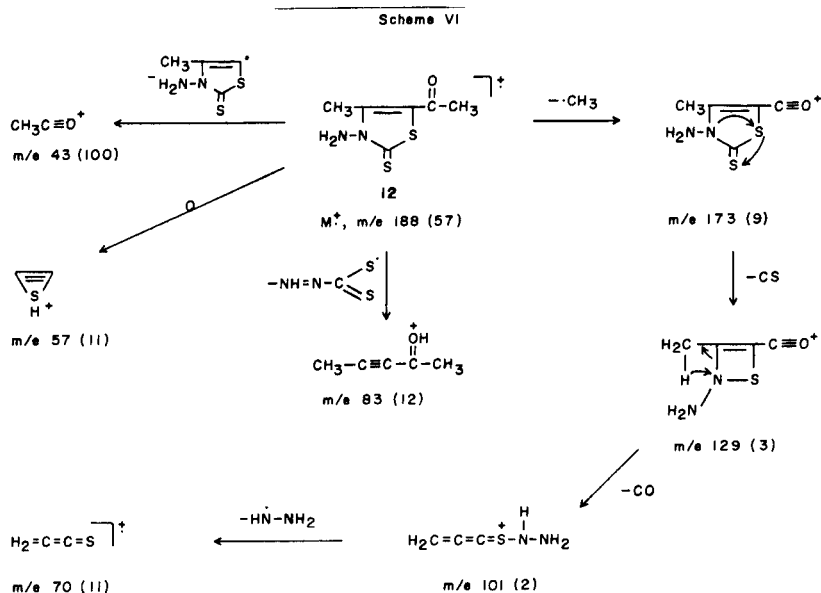


Scheme IV



Scheme V





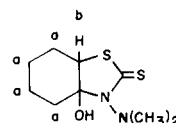
EXPERIMENTAL

The nmr spectra were obtained with a Varian T-60 nmr spectrometer. The chemical shifts are reported in ppm δ , using tetramethylsilane as reference. All melting points were taken upon a Fisher-Johns block and are uncorrected. The infrared spectra for **1**, **2**, **6**, **11**, and **12** were obtained with a Perkin-Elmer Model 21 spectrophotometer with a sodium chloride prism. The ultraviolet spectra for **11** and **12** were obtained using a Cary Model 11 spectrophotometer and matched 1-cm quartz cells. The electron impact mass spectra for **4**, **8**, **11**, and **12** were determined with a Varian-MAT CH-7A mass spectrometer operating at an ionizing potential of 70 eV using a direct insertion probe technique with a source temperature of 250°.

3a,4,5,6,7a-Hexahydro-3a-hydroxy-3-(dimethylamino)-2-benzothiazolinethione (1).

To a stirred solution containing 30 g (0.5 mole) of 1,1-dimethylhydrazine, 50 g of concentrated ammonium hydroxide and 200 ml of ethanol, 38 g (0.5 mole) of carbon disulfide was added dropwise at 0 to 10°. After

stirring at 25-30° for 1 hour, 66.3 g (1.0 mole) of 2-chlorocyclohexanone was added dropwise while maintaining the temperature at 5-15°. The reaction mixture was stirred at 25-30° for 3 days. After cooling to 5°, 2000 g of ice water was added and stirring continued at 0-10° for 1 hour. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. Crude **1**, mp 137-139°, was obtained in 92% yield. After recrystallization from ethanol, it melted at 142-143°; ir (potassium bromide): 3500-3100 (OH), 2950 (C-H), 1450 (CH_2 def), 1370 and 1333 (>N-C(=S)-S mode) cm^{-1} ; nmr (deuteriodimethylsulfoxide): δ 1.61-2.06 (m, 8, a), 3.50-3.75 and 3.75-4.03 (2m, 1, b), 3.20 (s, 6, -N(CH₃)₂),



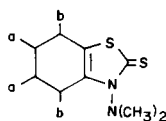
2.70 and 6.70 (2s, 1, OH) exchanged with deuterium oxide.

Anal. Calcd. for C₉H₁₆N₂OS₂: C, 46.52; H, 6.94; N, 12.06; O, 6.89; S, 27.60. Found: C, 46.54; H, 7.03; N, 11.88; O, 7.09; S, 27.43. Calcd. MW 232.4. Found: 234 (C₆H₆).

4,5,6,7a-Tetrahydro-3-(dimethylamino)-2-benzothiazolinethione (2).

To a stirred solution at 0° containing 60 g (1.0 mole) of 1,1-dimethylhydrazine and 1500 ml of diethyl ether, 66 g (1.0 mole) of powdered 85% potassium hydroxide was added in one portion. After stirring for 30 minutes, 83.4 g (1.1 moles) of carbon disulfide was added dropwise at 0-10° over a 1 hour period. The reaction mixture was stirred at 25-30° for 24 hours. The solid was collected by filtration, washed with 500 ml of diethyl ether and air-dried at 25-30°. The potassium dimethylaminodithiocarbamate [(CH₃)₂N-NH-C(=S)SK] was obtained in 95% yield and was used without further purification.

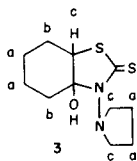
To a stirred slurry containing 43.6 g (0.25 mole) of the above potassium salt and 400 ml of ethanol, 33.2 g (0.25 mole) of 2-chlorocyclohexanone was added in one portion. After stirring for 35 minutes, the temperature had risen from 20° to 34°. The stirred reaction mixture was heated at reflux (78-80°) for 3 hours and then allowed to cool and stir at 25-30° for 24 hours. After cooling to 5°, 600 g of the water was added and stirring continued at 0-10° for 30 minutes. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. Crude **2**, mp 63-65°, was obtained in 80% yield. After recrystallization from heptane, it melted at 67.0-67.5°; ir (potassium bromide): 2950 (C-H), 1675 (C=C), 1445 (CH_2 def) and 1305 (>N-C(=S)-S) cm^{-1} ; nmr (deuteriochloroform): δ 1.51-1.94 (m, 4, a), 2.15-2.60 (m, 4, b), 3.18 (s, 6, -N(CH₃)₂).



Anal. Calcd. for $C_9H_{14}N_2S_2$: C, 50.53; H, 6.58; N, 13.07; S, 29.92. Found: C, 50.30; H, 6.70; N, 13.03; S, 29.72. Calcd. MW 214.4. Found: 216 (C_6H_6).

3a,4,5,6,7a-Hexahydro-3a-hydroxy-3-pyrrolidinyl-2-benzothiazolinethione (3).

To a stirred slurry containing 24.6 g (0.2 mole) of *n*-aminopyrrolidine hydrochloride and 200 ml of 2-propanol, 26.4 g (0.4 mole) of 85% potassium hydroxide was added in one portion. After stirring at 25-30° for 30 minutes and cooling to 5°, 15.2 g (0.2 mole) of carbon disulfide was added dropwise at 0-10°. After stirring at 25-30° for 5 hours and cooling to 0°, 26.6 g (0.2 mole) of 2-chlorocyclohexanone was added in one portion. The reaction mixture was stirred at 25-30° for 18 hours. To the stirred reaction mixture, 700 ml of water was added and stirring continued at 25-30° for 30 minutes. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. Crude **3**, mp 124-126°, was obtained in 87% yield. After recrystallization from isopropyl alcohol and heptane (1:1), it melted at 137.5-138.5°; nmr (deuteriodimethylsulfoxide): δ 1.09-1.96 (m, 8, a), 1.96-2.39 (m, 4, b), 3.09-3.94 (m, 5, c), 6.49 (s, 1, OH) exchanged with deuterium oxide.

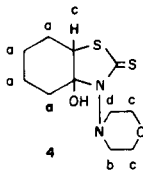


Anal. Calcd. for $C_{11}H_{18}N_2OS_2$: C, 51.13; H, 7.02; N, 10.84; O, 6.19; S, 24.82. Found: C, 51.12; H, 7.02; N, 10.72; O, 5.99; S, 24.62. Calcd. MW 258.4. Found: 262 ($CHCl_3$).

3a,4,5,6,7a-Hexahydro-3a-hydroxy-3-morpholino-2-benzothiazolinethione (4) and 3a,4,5,6,7a-Hexahydro-3a-hydroxy-3-piperidino-2-benzothiazolinethione (5).

The potassium morpholino or piperidinodithiocarbamates were prepared in 95% yields by the same procedure described for potassium dimethylaminodithiocarbamate except the 1,1-dimethylhydrazine was substituted with either *N*-aminomorpholine or *N*-aminopiperidine. The salts were used without any further purification.

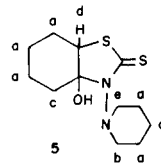
To a stirred slurry at 15° containing 0.2 mole of either potassium morpholino or piperidinodithiocarbamate in 270 ml of ethanol, 26.6 g (0.2 mole) of 2-chlorocyclohexanone was added in one portion. The stirred reaction mixture was maintained at 25-30° for 24 hours. After cooling to 10°, 600 g of ice water was added and stirring continued at 10-15° for 30 minutes. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. Crude **4**, mp 173-175°, and crude **5**, mp 151-152°, were obtained in 84 and 90%, respectively. Compound **4** melted at 175-176° after recrystallization from ethyl acetate and DMF (5 g-400 ml of ethyl acetate + 200 ml of DMF). The melting point of **5** remained unchanged after recrystallization from ethyl acetate; **4**, nmr (deuteriodimethylsulfoxide): δ 1.85-2.35 (m, 8, a), 2.57-3.02 (m, 2, b), 3.30-4.00 (m, 5, c), 4.00-4.76 (m, 2, d), 6.54 (s, 1, OH) exchanged with deuterium oxide;



electron impact mass spectrum: m/e (relative intensity) M^+ : 274 (3), 256 (2) (M^+-H_2O), 190 (10), 171 (10), 144 (38), 130 (37), 101 (12), 97 (11), 86 (100) and 85 (32).

Anal. Calcd. for $C_{11}H_{18}N_2O_2S_2$: C, 48.14; H, 6.61; N, 10.21; O, 11.66; S, 23.37. Found: C, 47.96; H, 6.58; N, 10.02; O, 11.88; S, 23.10.

Compound **5** nmr (deuteriodimethylsulfoxide): δ 0.90-1.83 (m, 12, a), 1.90-2.41 (m, 2, b), 2.68-3.17 (m, 2, c), 3.28-3.52 (m, 1, d), 3.91-4.40 (m, 2, e),

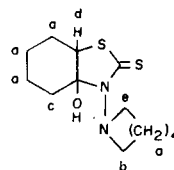


6.49 (s, 1, OH) exchanged with deuterium oxide.

Anal. Calcd. for $C_{12}H_{20}N_2OS_2$: C, 52.94; H, 7.40; N, 10.28; O, 5.87; S, 23.54. Found: C, 53.05; H, 7.54; N, 10.40; O, 5.71; S, 23.45.

3,4,5,6,7a-Hexahydro-3a-hydroxy-3-(hexahydro-1*H*-azepinyl)-2-benzothiazolinethione (6).

To a stirred solution at 5° containing 70.6 g (0.5 mole) of *N*-aminohomopiperidine, 50 g of concentrated ammonium hydroxide and 300 ml of ethanol, 38 g (0.5 mole) of carbon disulfide was added dropwise at 0-10°. After stirring at 25-30° for 1 hour and cooling to 5°, 66.3 g (0.5 mole) of 2-chlorocyclohexanone was added in one portion. The stirred reaction mixture was maintained at 25-30° for 3 days. The reaction mixture was poured into 2000 g of ice water and stirred at 0-10° for 30 minutes. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. Crude **6**, mp 141-143°, was obtained in 96% yield. After recrystallization from ethanol, it melted at 151-152°; ir (potassium bromide): 3600-3100 (OH), 2950 and 2860 (C-H), 1450 (CH_2 def), 1332 and 1308 ($>N-C(=S)-S-$ mode) cm^{-1} ; nmr (deuteriodimethylsulfoxide): δ 1.00-1.92 (m, 14, a),



1.92-2.57 (m, 2, b), 2.80-3.26 (m, 2, c), 3.26-3.57 (m, 1, d), 3.75-4.12 (m, 2, e), 6.37 (s, 1, OH) exchanged with deuterium oxide.

Anal. Calcd. for $C_{13}H_{22}N_2OS_2$: C, 54.50; H, 7.74; N, 9.78; O, 5.59; S, 22.39. Found: C, 54.70; H, 7.70; N, 9.66; O, 5.79; S, 22.29.

4,5,6,7-Tetrahydro-3-pyrrolidinyl-2-benzothiazolinethione (7), 4,5,6,7-Tetrahydro-3-morpholino-2-benzothiazolinethione (8), 4,5,6,7-Tetrahydro-3-piperidino-2-benzothiazolinethione (9) and 4,5,6,7-Tetrahydro-3-(hexahydro-1*H*-azepinyl)-2-benzothiazolinethione (10).

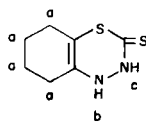
A stirred slurry comprising 0.2 mole of **3**, **4**, **5**, or **6**, 2 g of *p*-toluenesulfonic acid monohydrate, and 200 ml of benzene was heated at reflux for 3 hours or until 2.7 ml of water was collected. Benzene (160 ml) was removed by distillation. To the cooled residue at 30°, 100 ml of petroleum ether was added and the slurry stirred at 0-10° for 30 minutes. The solid was collected by filtration and air-dried at 25-30°. The data are summarized in Table 1.

5,6,7,8-Tetrahydro-1*H*-4,1,2-benzothiadiazine-3(2*H*)-thione (11).

Potassium dithiocarbamate was prepared by the method described by Busch and Starke [3]. A charge containing 66 g (1.0 mole) of 85% potassium hydroxide and 800 ml of 2-propanol was stirred for 15 minutes or until a solution resulted. After cooling the stirred solution to 0°, 33.8 g (1.0 mole) of 95% hydrazine was added in one portion, followed by the dropwise addition of 76 g (1.0 mole) of carbon disulfide at 0-10°. The reaction mixture was stirred at 25-30° for 24 hours. The solid was collected

by filtration, washed with 800 ml of 2-propanol and air-dried at 25-30° for only 3 hours. If the potassium dithiocarbazate is allowed to dry longer than 3 hours, it decomposes. The potassium dithiocarbazate was obtained in 98% yield and was used without any further purification.

To a stirred slurry comprising 43.9 g (0.3 mole) of freshly prepared potassium dithiocarbazate and 300 ml of ethanol, 39.8 g (0.3 mole) of 2-chlorocyclohexanone was added in one portion. After stirring for 25 minutes, the temperature rose from 24 to 44°. The stirred reaction mixture was heated at reflux (78-80°) for 3 hours, then allowed to cool and stir at 25-30° for 18 hours. After cooling to 0°, 600 g of ice water was added and stirring continued at 0-10° for 30 minutes. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. The crude product (48 g), mp 100-110°, contains **11** which is soluble in dilute sodium hydroxide and an unidentified polymer. Attempts to separate **11** from the polymer by the sodium hydroxide-hydrochloric acid treatment proved partially successful. Under these conditions, only a small amount of **11** could be recovered. The alkali-acid sensitivity of **11** containing the polymer excluded this treatment for the separation of **11** from the polymer. The separation can be effected by recrystallization from ethyl acetate. Thus 48 g of crude **11** was recrystallized from 240 ml of ethyl acetate to give 16.8 g of **11** (30% yield), mp 136-137°; ir (potassium bromide): 3216 (NH of secondary NH), 2939 (CH₂ asym), 2860 (CH₂ sym), 1654 (C=C), 1449 (CH₂ deform), 1301 (>N-C(=S)-S- mode) and 1086 (C=S) cm⁻¹; electron impact mass spectrum: m/e (relative intensity) M⁺: 186 (67), 110 (20), 93 (111), 81 (100), 76 (9) and 59 (14); nmr (deuteriochloroform): δ 1.00-3.02 (m, 8, a), 3.48-4.02 (m, 1, b), 10.68 (br s, 1, c);



11 was titrated potentiometrically in 2-propanol with (C₄H₉)₄NOH, equivalent weight found: 182, calculated or theory: 186. The uv spectral data also confirmed the proposed structure for **11**.

a, = 81.7 at 323 mμ in methanol

a, = 44.6 at 325 mμ in methanol + sodium hydroxide

Anal. Calcd. for C₇H₁₀N₂S₂: C, 45.13; H, 5.41; N, 15.04; S, 34.42. Found: C, 45.30; H, 5.52; N, 15.14; S, 34.50.

5-Acetyl-3-amino-4-methyl-4-thiazoline-2-thione (**12**).

To a stirred slurry comprising 146.3 g (1.0 mole) of freshly prepared potassium dithiocarbazate and 1000 ml of ethanol, 134.5 g (1.0 mole) of 3-chloro-2,4-pentanedione [4] was added in one portion. An exothermic reaction set in causing a temperature rise from 23° to 54° over a 1 minute period. The stirred reaction mixture was heated at reflux (78-80°) for 3 hours and then allowed to stir at 25-30° for 24 hours. After cooling to 0°, 1000 g of ice water was added and stirring continued at 0-10° for 30 minutes. The solid was collected by filtration, washed successively with water until neutral, then with 250 ml of heptane and air-dried at 25-30°. Crude **12**, mp 154-157°, was obtained in 76% yield. After recrystallization from ethanol-ethyl acetate (1:1), it melted at 170.0-170.5°; nmr (deuteriodimethylsulfoxide): δ 2.47 (s, 3, CH₃C=), 2.65 (s, 3, -COCH₃), 6.10 (br s, 2, -NH₂). The uv spectral data also supported the proposed structure for **12**; uv (methanol): a, = 93.4 at 353 mμ (no changed with sodium hydroxide). In addition **12** would not titrate with 0.1N tetrabutylammonium hydroxide. Electron impact mass spectrum: m/e (relative intensity) M⁺: 188 (57), 173 (9), 129 (3), 101 (2), 83 (12), 70 (11), 57 (11), and 43 (100); ir (potassium bromide): 3227 and 3141 (H bonded NH of NH₂), 2992 (CH), 1676 (C=O), 1650 (C=C), 1606 (NH₂ deform), 1557 (ν mode of thiazoline ring), 1377 and 1370 (CH₃ deform), 1276 and 1234 (>N-C(=S)-S- mode) and 1174 (C=S) cm⁻¹.

Anal. Calcd. for C₈H₈N₂OS₂: C, 38.27; H, 4.28; N, 14.88; O, 8.50; S, 34.06. Found: C, 38.25; H, 4.35; N, 14.85; O, 8.66; S, 33.86.

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