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Studies of Heterocyclic Compounds. VI.[1] The Reactions of 5,6-Dihydrothiazolo[2,3-*b*]thiazolium Salts with O- and S-Nucleophiles

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The reaction of 5,6-dihydrothiazolo[2,3-*b*]thiazolium salts (**1**) with hydroxide ion furnished disulfide of 3-(2-mercaptoethyl)-4-thiazolin-2-one (**6**). The reaction of **1** with hydrogensulfide ion furnished 3-(2-mercaptoethyl)-4-thiazolin-2-thione (**7**) and/or its disulfide (**8**) and with N,N-dimethyldithiocarbamate ion furnished 3-(N,N-dimethyldithiocarbamylethyl)-4-thiazolin-2-thione (**12**) whereas the reaction of **1b** with thiophenolate ion afforded 3-(2-phenylthioethyl)-4-thiazolin-2-thione (**18b**), thiazole (**21**), **6b**, phenyl 2-[2-(4-phenylthiazolin-2-thion-3-yl)ethylthio]ethyl disulfide (**22**) and phenyl 2-phenylthioethyl disulfide (**23**). Brief reaction mechanism of the formation of these products are discussed. The reaction of **1** is considered to be initiated by the attack of the nucleophile on the polarized $>C=\overset{+}{N}<$bond to form an adduct and to proceed through *AE*-mechanism. The elimination stage of the reaction is concluded to depend upon basicity, polarizability and other properties of the reagent to induce either the cleavage of S_7-C_{7a} bond, the cleavage of S_7-C_{7a} and N-C_5 bonds, or another attack of the reagent on C_6 or on S_7.

It has previously been reported that the carbonium ions stabilized by three adjacent hetero-atoms (S, S, and N) such as N,N-dimethyl-S,S′-dimethyldithiocarbamidium ion,[3] 3-dimethylamino-1,3-dithiolanylium ion,[4] 3-methyl-2-methylthio-2-thiazolinium ion,[5] and 2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium ion[5a,6] reacted with several nucleophiles and had a general tendency to react with one kind of nueleophile in one direction and, therefore, not to be able to yield more than one product which might be formed by the attack of one kind of nucleophile on two sites. 5,6-Dihydrothiazolo[2,3-*b*]thiazolium cation (**1**) is one of those carbonium ion but differs from previously reported compounds in their aromaticity, so we are interested in its reactivity with nucleophiles. In the preceding paper, it was described that **1** could readily be synthesized from 2-mercaptothiazoline and α-haloketones, and was

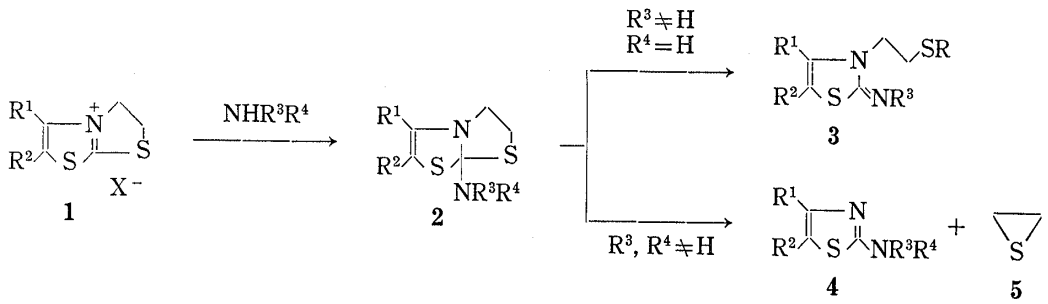
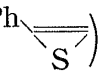


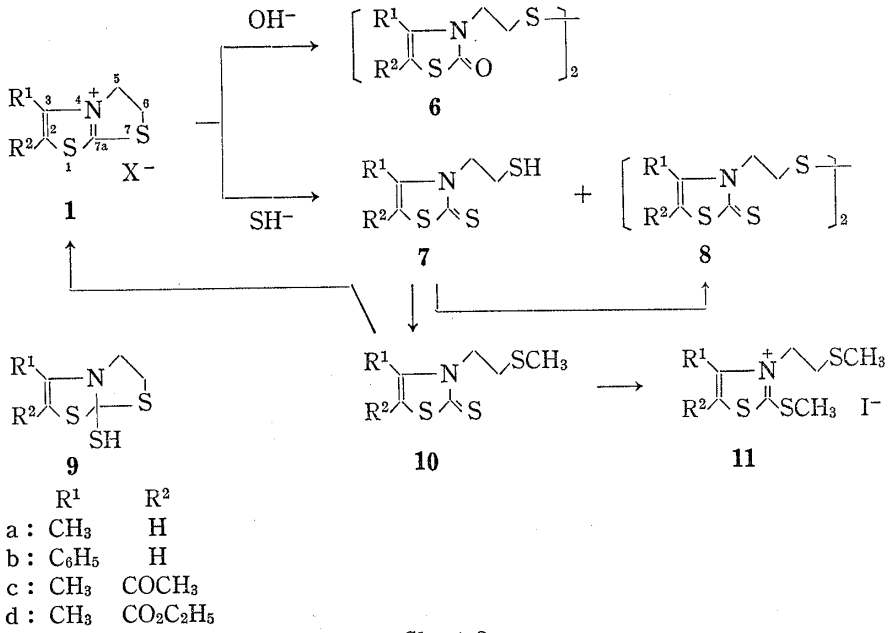
Chart 1

1) Part V: H. Ohtsuka, H. Toyofuku, T. Miyasaka, and K. Arakawa; *Chem. Pharm. Bull.* (Tokyo), **23**, 3234 (1975).
2) Location: *1-5-8, Hatanodai, Shinagawa-ku, Tokyo, 142, Japan.*
3) T. Nakai, M. Okawara, *Bull. Chem. Soc. Japan*, **43**, 3528 (1970); J.L. Richards, D.S. Tarbell, and E.H. Hoffmeister, *Tetrahedron*, **24**, 6485 (1968); H. Rintelen and O. Riester, *C.A.*, **51**, 7913 (1957).
4) T. Nakai, Y. Ueno, and M. Okawara, *Bull. Chem. Soc. Japan*, **43**, 156 (1970); T. Nakai and M. Okawara, *Bull. Chem. Soc. Japan*, **43**, 1864 (1970).
5) *a*) T. Nakai, *Yuki Gosei Kagaku Kyokai Shi*, **28**, 708 (1970); *b*) A.D. Clark and P. Sykes, *J. Chem. Soc.*, **1971**, 103.
6) S. Seto and Y. Ikegami, *Bull. Chem. Soc. Japan*, **36**, 730 (1963).

attacked by amines at C-7a to form the unstable adduct **2** which, in the case of primary amines, was immediately transformed into 4-thiazolin-2-imine (**3**), but in the case of secondary amines which could be isolated and collapsed into 2-aminothiazole (**4**) and thiirane (**5**) in solution.[1] This paper describes the reaction of **1** with oxygen- and sulfur-nucleophile to furnish several products which are seemingly formed by the attack of nucleophiles on several sites.

It is known that on reaction with hydroxide ion thiazolium salts result in destruction of the ring or give 2-oxo-derivatives,[7] that 2-alkylthio-3-alkyl-thiazolium salts give 2-thiazolidinones,[5] and that 2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium salt gives disulfide of 3-(2-mercaptoethyl) thiazolidin-2-one.[6] Bradsher and Jones have already proposed tentatively a dimeric structure **6a** for the product obtained by treatment of **1a** with sodium hydroxide.[8] In the present study, the reaction of **1a—c** with hydroxide ion gave disulfide (**6a—c**), formed by opening of the thiazoline ring followed by the oxidation of the resulted mercaptan. The structure of **6b** was determined by elemental and spectral analyses. The mass spectrum exhibited a molecular peak at *m/e* 472 very weakly, a base peak at *m/e* 236 ($M^+/2$, fission of S–S bond), and a structurally consistent fragmentation pattern *m/e* 204 ($M^+/2-S$), 176 ($M^+/2-$ ), 134 (), 102 (Ph–C≡CH), so the composition of **6b** doubled $C_{11}H_{10}ONS_2$ which was led from the elemental analysis of **6b**. It was known that **6b** was symmetrical compound by the nuclear magnetic resonance (NMR) spectrum which showed A_2B_2 pattern centered at δ 2.52 (4H) and 3.86 ppm (4H), a singlet at δ 5.96 ppm (2H), and a complex multiplet centered at δ 7.39 ppm (10H). The IR spectrum showed a carbonyl band at 1660 cm^{-1}.

5,6-Dihydrothiazolo[2,3-*b*]thiazolium salt (**1**) was treated with sodium hydrogensulfide in absolute ethanol to give 2-(thiazolin-2-thion-3-yl)ethylmercaptan (**7**) and/or its disulfide (**8**). The possibility that the product might be an isomeric simple adduct **9** rather than **7** was denied by the following evidence. The NMR spectrum of **7** exhibited the presence of $-CH_2CH_2SH$ and the ultraviolet (UV) spectra of **7** and **8** were analogous to that of 3-alkyl-substituted thiazolin-2-thione.[9] Mercaptan (**7**) was smoothly oxidized by hydrogen peroxide to afford disulfide (**8**) and when treated with iodomethane (1 eq. mole) in the presence of base



	R^1	R^2
a :	CH_3	H
b :	C_6H_5	H
c :	CH_3	$COCH_3$
d :	CH_3	$CO_2C_2H_5$

Chart 2

7) A. Schoberlin and M. Stock, *Ber.*, **73**, 1240 (1940); G.M. Clark and P. Sykes, *J. Chem. Soc.*, 1967, 1269.
8) C.K. Bradsher and W.J. Jones, Jr., *Rec. Trav. Chim. Pays-Bas*, **87**, 274 (1968).
9) G. Kjellin and J. Sandstrom, *Acta Chim. Scand.*, **23**, 2888 (1969).

gave methylsulfide (**10**) in quantitative yield. 4-Phenyl derivative (**10b**), when treated with excess iodomethane, gave thiazolium salt (**11b**), but 5-acetyl derivative (**10c**) gave an unexpected product **1c**. Because **10c** has an intensely electron-withdrawing group on the thiazole ring, the conversion of **10c** to **1c** is probably best envisaged as methylation on sulfur of N_3-side chain rather than that of C_2-thioketone, followed by cyclization with concerted elimination of dimethylsulfide. Methylsulfide (**10c**) was also transformed by treatment with 47% aqueous hydrobromic acid into **1c**, but **10b** was not. Hydrogensulfide was known from foregoing results to attack at either C-6, or C-7a of **1**.

The thiazolium salt (**1c**) reacted with N,N-dimethyldithiocarbamate ion to afford crystals, $C_{11}H_{16}ON_2S_4$, mp 171—173° in 43% yield. The structure of this compound was determined by spectroscopic data as **12c** formed by the attack of the nucleophile on C-6 rather than as **13c** which might be produced if the nucleophile attacked at C-7a. The NMR spectrum showed A_2B_2 pattern centered at δ 3.68 and 4.88 ppm due to the methylene protons on C_5 and C_6.[10] The UV spectrum was analogous to a curve composed by addition of that of methyl N,N-dimethyldithiocarbamate[11] to that of **10c**.

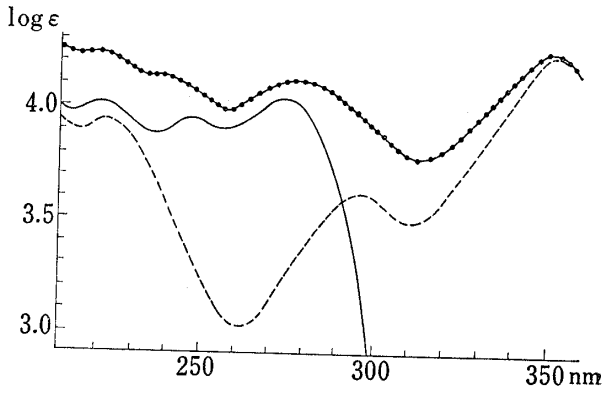
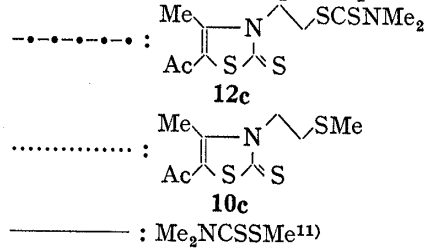


Fig. 1. Ultraviolet Absorption Spectra (in MeOH)



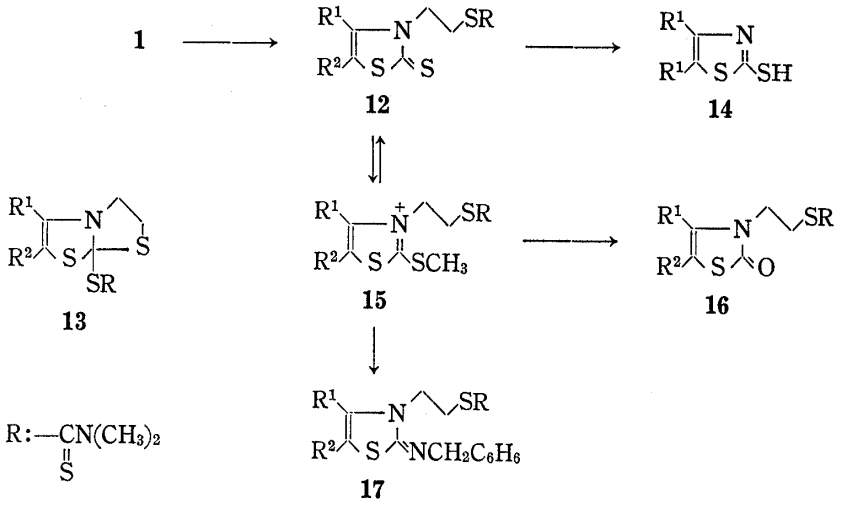


Chart 3

On reaction of **1a**, **1b**, and **1d** with N,N-dimethyldithiocarbamate ion in ethanol the sole product which could be isolated was also **12**, the structure of which was further confirmed by the following chemical behaviors. Although **12** resisted usual acidic and alkaline hydrolysis, on heating at 130° with potassium hydroxide in ethylene glycol **12** yielded 2-mercaptothiazole

10) The NMR spectrum of the compound **2** formed by the addition of secondary amines on C-7a of the compound **1** exhibited fairly complex peaks at the range of δ 2.81—4.28 ppm.
11) H.P. Koch, *J. Chem. Soc.*, **1942**, 401.

(**14**) and by treating with iodomethane afforded 2-methylthiothiazolium salt (**15**) irrespectively of substituents. Thiazolium salt (**15**) was treated with hydrogensulfide ion to be transformed into **12**, with hydroxide ion to give 2-thiazolone (**16**) ($\nu_{C=O}$ 1645 cm^{-1}), and with benzylamine

Table I. Physical Properties of 4-Thiazolin-2-thiones

No.	R^1	R^2	R^3	yield (%)	mp (°C)	$\nu_{C=S}$ cm^{-1}	δ_{C_5-H}[a] ppm	$\delta_{C_4-CH_3}$[a] ppm	λ_{max}[b] nm (log ε)
12a	CH_3	H	$SCSN(CH_3)_2$	57.7	129—130	1147[c] 1165	6.20	2.44	243 (4.03) 277 (4.01) 321.5(4.10)
12b	C_6H_5	H	$SCSN(CH_3)_2$	64.0	128	1146[c] 1158	6.93		235 (4.15) 278.8(4.09) 322.2(4.12)
12c	CH_3	$COCH_3$	$SCSN(CH_3)_2$	43.5	171—173	1160[c]		2.37	220 (4.22) 242 (4.10) 278.5(4.09) 353.5(4.24)
12d	CH_3	$CO_2C_2H_5$	$SCSN(CH_3)_2$	65.0	140—140.5	1150[c] 1186		2.63	217.6(4.25) 244 (4.07) 278 (4.10) 340.5(4.28)
18a	CH_3	H	SC_6H_5	22.3	oil	1159[d]	6.12	2.17	252.5 321.5
18b	C_6H_5	H	SC_6H_5	32.0	120—121	1157[c]	6.43		252 (3.97) 322.5(4.41)
18c	CH_3	$COCH_3$	SC_6H_5	28.0	78.5—80	1152[c]		2.29	252.7(3.89) 295 (5.59) 353.5(4.21)

a) in deuteriochloroform *b*) in methanol *c*) in KBr tablet *d*) in chloroform

Table II. Physical Properties of 2-Methylthiothiazolium Iodide

No.	R^1	R^2	R^3	mp (decomp.)	δ_{C_5-H}[a] ppm	$\delta_{C_4-CH_3}$[a] ppm	λ_{max}[b] nm (log ε)
15a	CH_3	H	$SCSN(CH_3)_2$	133—142	7.77	2.62	218.8 (4.40) 243 sh (3.95) 283.5 (4.08) 298 sh (4.02)
15b	C_6H_5	H	$SCSN(CH_3)_2$	107—110	8.08		216 (4.59) 243 sh (4.19) 283.5 (4.11) 300 (4.05)
15c	CH_3	$COCH_3$	$SCSN(CH_3)_2$	79—81		2.68 or 2.91	219.6 (4.44) 241 sh (4.11) 276.5 (4.06) 315 (3.93)
15d	CH_3	$COOC_2H_5$	$SCSN(CH_3)_2$	137—141		2.90	282 (4.42)
19a	CH_3	H	SC_6H_5	118—125	7.77	2.51	217.8 (4.34) 250 (3.80) 296.7 (3.96)
19b	C_6H_5	H	SC_6H_5	107—110	8.04		214 sh (4.49) 247 sh (4.02) 297.5 (4.01)
19c	CH_3	$COCH_3$	SC_6H_5	116—117		2.62 ro 2.80	218.5 (4.40) 251.4 (3.00) 308.5 (4.06)

a) in DMSO-d_6 *b*) in MeOH

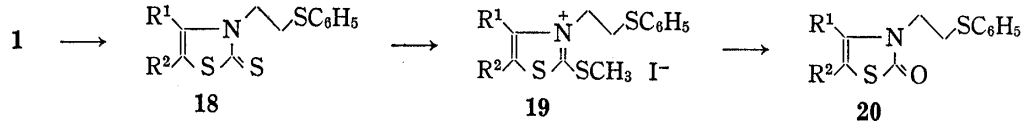


Chart 4

to furnish thiazolin-2-benzylimine (**17**), mp 90.5—91°. The liberation of methylmercaptan was observed during these reactions. Since the C_5-H signal was shifted from δ 6.93 ppm to 8.08 ppm, the methylation of **12** took place on sulfur of C_2-thioketone moiety rather than that of dithiocarbamate in the side chain, as indicated in Table I and II. By treatment of **1** with thiophenolate ion in absolute ethanol there was obtained 2-(4-thiazoline-2-thion-3-yl)ethyl phenyl sulfide (**18**) as the major product. Ethyl phenyl sulfide (**18**), when methylated, afforded thiazolium salts (**19**), which was hydrolyzed by alkali to yield 2-thiazolone (**20**) ($\nu_{C=O}$ 1660 cm^{-1}) with liberation of methylmercaptan. The structure of **18** was established by spectroscopy. For instance, **18** had λ_{max} 250 nm in the UV spectrum analogous to that of phenyl alkyl sulfide[12] besides corresponded to that of 3-alkyl-substituted-4-thiazolin-2-thione (See Table I). The signals of C_5–H and C_4–Me of **19** were shifted to lower field than those of **18**, so thiazole ring of **19** was quarternarized (Table I, II).

Because the yield of **18** was low as shown in Table I and several other products were found on thin-layer chromatography (TLC), we have minutely investigated the products from **1b** and thiophenolate ion. By treating with sodium thiophenolate in absolute ethanol at room temperature, **1b** gave 17% of 4-phenylthiazole (**21**), 11.6% of bis[2-(2-oxo-4-phenylthiazolin-3-yl)ethyl disulfide (**6b**) , 6.2% of thiazolin-2-one (**22**), and trace of disulfide (**23**) in addition to 32% of **18b**. The spectroscopic data of 4-phenylthiazole (**21**) are in good agreement with those described in the literature.[13] A composition of $C_{19}H_{19}ONS_4$ was suggested by the mass spectrum of **22** and confirmed by elemental analysis. The structure of **22** was determined by the carbonyl band at 1659 cm^{-1} in the infrared (IR) spectrum, multiplets at δ 2.4—3.2 ppm ($3\times CH_2$, adjacent to sulfur) in the NMR spectrum, and fragment peaks of *m/e* 405 (M^+), 266 (M^+—SPh), 236 (M^+—$\overset{+}{S}$–SPh), 169($\left[\overset{+}{S}\text{–SPh}\right]$), and 141 (SSPh) in the mass spectrum. There was obtained a trace amount of **23**, the structure of which was inferred by spectroscopic data. The NMR spectrum showed two singlets at δ 2.41 and 7.12 ppm (intensities 2: 5) and the mass spectrum showed peaks of *m/e* 278, 109, and 77. The UV spectrum was analogous to those of phenyl methyl sulfide and phenyl methyl disulfide.[12,14]

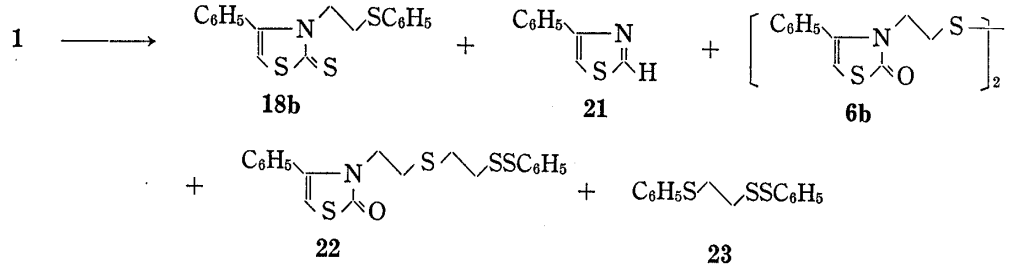


Chart 5

Plausible mechanism for the formation of these compounds **6**, **18**, and **21**—**23** may be described as follows (Chart 6). By the attack of thiophenolate ion on C_{7a}, **1b** gives an adduct **24a** which is too unstable to isolate. The adduct **24a** is attacked by the second thiophenolate ion upon two sites, C-6 (path a) and S-7 (path b). In the path a, the adduct is attacked on C_6 followed by cleavage of C_6–S_7 bond and simultaneously with formation of thioketone leaves

12) E.A. Fehnel, *J. Am. Chem. Soc.*, **71**, 84 (1949).
13) J. McLean and G.D. Muir, *J. Chem. Soc.*, **1942**, 385.
14) P.H. Koch, *J. Chem. Soc.*, **1940**, 394.

thiophenolate ion from C_{7a} to give phenyl sulfide (**18b**). In the path b, the adduct is attacked by the second thiophenolate ion on S_7 as shown by dotted line to form the carbanion (**25**) which is stabilized by the two neighboring sulfurs and the nitrogen. The carbanion (**25**) is protonated followed by concerted elimination of 1-phenylthiothiiranium cation (**26**) and thiophenolate ion. This step will be favored by resonance stabilization of thiazole ring in **21** so formed. The reaction of thiiranium cation (**26**) so formed with **24b** leaves thiazolium ion (**27**), which is hydrolyzed by alkali during the after-treatment to be transformed into 2-thiazolone (**22**). Phenyl ethyl disulfide (**23**) seems to be produced from thiiranium cation

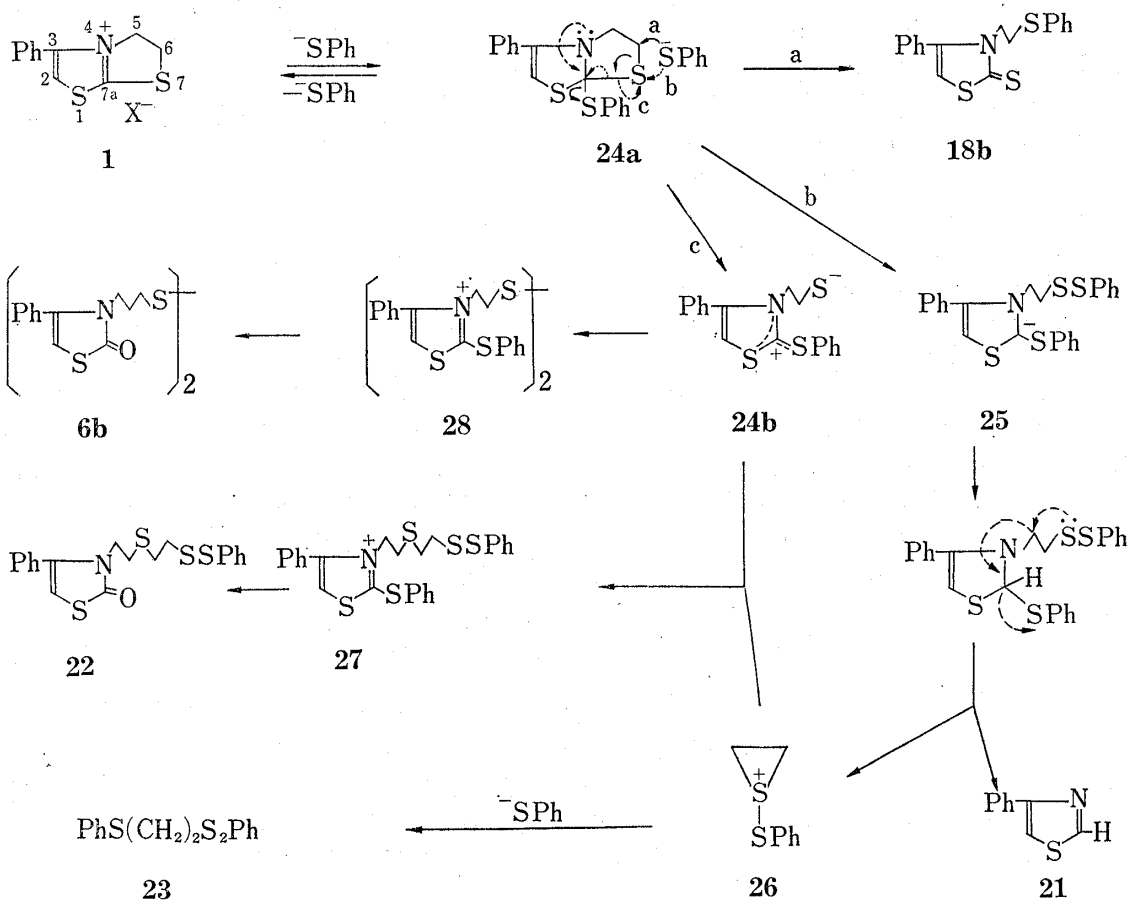


Chart 6

(**26**) and thiophenolate ion. Compound **6b** is arisen from hydrolysis of disulfide (**28**) which is formed by oxidation of **24b**, as well as thiazolium cation (**27**). But the following possible alternatives for the formation of **18b** and **6b** cannot be eliminated: thiophenolate ion directly attacks on C_6 to afford **18b** and the remaining **1b** is hydrolyzed by alkali during the after-treatment to furnish **6b**.

Using the thiocyanate ion as a nucleophile there was obtained thiocyanate salt of **1** as a sole product. No reaction occurred on the ring of **1** with thiocyanate ion. It seemed that because thiocyanate salt of **1** was too stable to react with another thiocyanate ion, and practically the salt (**1**; X=SCN) was difficult to react with even amines. On reaction of dithiazolium cation with thiocyanate ion it has been reported that only the anion-exchange occurred.[15]

On the basis of the above mentioned results and of the evidences described in the preceding paper, the following mechanism is now proposed on the reaction of 5,6-dihydrothiazolo[2,3-*b*]-

15) J.Z. Oliver, B.A. Bierl, and J.M. Ruth, *J. Org. Chem.*, 37, 131 (1972).

thiazolium salt with nucleophiles. The reaction is initiated by the addition of the nucleophile upon C_{7a} to form an unstable intermediate which is readily transformed into more stable secondary product except in the case of the secondary amine-adduct. If the added nucleophile contains another proton which is abstracted under the reaction conditions (when hydroxide ion, primary amines or hydrosulfide ion is applied as the nucleophile), rupture of the C_{7a}–S_7 bond is induced with re-aromatization of the thiazolium ring to form 3-(2-oxo-, 2-imino- or 2-thio-thiazolin)-ylsulfide anion, which either dimerizes by air oxidation or protonates to give thiazolin-2-one, -imine or -thione. In the case of the adduct of secondary amines the rupture of C_{7a}–S_7 bond occurs at higher temperature with simultaneous elimination of thiirane to form N,N-dialkylaminothiazole. If the applied nucleophile is intensely polar like N,N-dimethyldithiocarbamate, or thiophenolate ion, the nucleophile is able to behave as a leaving group at the same time and the adduct is susceptible to another attack of the reagent upon C_6 or upon S_7 with concerted elimination of the initially added nucleophile from the sp_3 carbon to furnish thiazolin-2-thione and thiazole.

Experimental[16]

Bis[2-(2-oxo-4-methylthiazolin-3-yl)ethyl] Disulfide (6a)——Compound **1a** (476 mg) was dissolved in 5% NaOH (5 ml) and allowed to stand to separate crystals. After standing for 5 days the crystals were collected by filtration to yield 240 mg of **6a** (69%) mp 80—81.5°. IR ν_{max}^{KBr} cm^{-1}: 1655. NMR (in $CDCl_3$): 2.17 (d, 3H), 2.98 (m, 2H), 3.98 (m, 2H), 5.73 (q, 1H). *Anal.* Calcd. for $C_{12}H_{16}O_2N_2S_4$: C, 41.38; H, 4.63, N, 8.04. Found: C, 41.16; H, 4.58; N, 8.11.

Bis[2-(2-oxo-4-phenylthiazolin-3-yl)ethyl] Disulfide (6b)——Into a stirred ice-cold solution of **1b** (598 mg) in H_2O (5 ml) there was added a solution of K_2CO_3 (138 mg) in H_2O (3 ml). The solution soon emulsified and deposited white crystals. After standing for 2 hr the crystals were collected by filtration. The mother liquor was kept in a refrigerator to give more crystals. The total crystals weighed 280 mg, 60%, mp 112—113°. IR ν_{max}^{KBr} cm^{-1}: 1660, 1448, 1388, 1266, 772. UV λ_{max}^{MeOH} nm (log ε): 250 sh (4.08). Mass Spectrum *m/e*: 236, 204, 176, 134. NMR (in $CDCl_3$) δ: 2.53 (double d, 4H), 3.86 (double d, 4H), 5.96 (s, 2H), 7.2—7.6 (m, 5H). *Anal.* Calcd. for $C_{22}H_{20}O_2N_2S_4$: C, 55.93; H, 4.27; N, 5.93. Found: C, 56.12; H, 4.17; N, 5.95.

Bis[2-(5-acetyl-4-methyl-2-oxo-thiazolin-3-yl)ethyl] Disulfide (6c)——Into a stirred ice-cold solution of **1c** (3.323 g) in H_2O (20 ml) there were added portionwise $CHCl_3$ (20 ml) and $NaHCO_3$ (1.27 g). After stirring for 30 min the $CHCl_3$ layer was separated and the aqueous layer was extracted with $CHCl_3$ (10 ml×3). The extracts were combined with the first $CHCl_3$ layer, dried, and evaporated to dryness. The residue crystallized from benzene–*n*-hexane (1: 1) to yield 1.04 g of **6c**. The mother liquor was evaporated and purified by chromatography on SiO_2 to give 213 mg of **6c** (56%). The analysis sample was obtained by recrystallization from benzene–*n*-hexane, mp 149—149.5°. UV λ_{max}^{MeOH} nm (log ε): 212.0 (3.96), 301.8 (4.36). IR ν_{max}^{KBr} cm^{-1}: 1665, 1635, 1570. NMR (in $CDCl_3$) δ: 2.37 (s, 3H), 2.64 (s, 3H), 3.03 (m, 2H), 4.12 (m, 2H). *Anal.* Calcd. for $C_{16}H_{20}O_4N_2S_4$: C, 44.45; H, 4.66; N, 6.48. Found: C, 44.41; H, 4.71; N, 6.54.

Bis[2-(4-methylthiazolin-2-thion-3-yl)ethyl Disulfide (8a)——To an ethanolic suspension of **1a** (952 mg) was added NaSH–EtOH (prepared from 92 mg Na in 20 ml EtOH saturated with H_2S). After stirring overnight the separated crystals (455 mg) were filtered and the filtrate was condensed to yield crystals (370 mg). The combined crystals were washed with water and recrystallized from large quantity of MeOH to afford 740 mg of **8a** (98%), mp 161—163°. IR ν_{max}^{KBr} cm^{-1}: 1570, 1422, 1340, 1308, 1252, 1174, 1162, 961. UV λ_{max}^{MeOH} nm: 320. NMR (in DMSO-d_6) δ: 2.34 (d, 6H), 3.13 (m, 4H), 4.40 (m, 4H), 6.68 (q, 1H). *Anal.* Calcd. for $C_{12}H_{16}N_2S_6$: C, 37.88; H, 4.23; N, 7.36. Found: C, 37.82; H, 4.25; N, 7.42.

3-(2-Mercaptoethyl)-4-methyl-4-thiazolin-2-thione (7a) and Its Disulfide (8a)——The mixture of pyridine (10 ml) and EtOH (10 ml) was saturated with H_2S, **1a** (714 mg) was added, and the mixture was stirred overnight. The solvent was removed and co-evaporated with EtOH (4 time) to furnish a solid which was crystallized from MeOH. **8a**, 40 mg (7%), mp 163—165°. The filtrate was condensed and purified by chromatography on SiO_2 to give 515 mg of **7a** as a syrup, (90%). IR ν_{max}^{KBr} cm^{-1}: 2930, 2420, 1585, 1440, 1364. NMR (in $CDCl_3$) δ: 1.48 (t, 1H, J=9 Hz), 2.33 (d, 3H, J=1 Hz), 2.93 (m, 2H), 4.28 (double d, 2H), 6.26 (q, 1H, J=1 Hz). *Anal.* Calcd. for $C_6H_9S_3N$: C, 37.70; H, 4.75; N, 7.33. Found: C, 38.01; H, 4.75; N, 7.40.

3-(2-Mercaptoethyl)-4-phenyl-4-thiazolin-2-thione (7b) and Its Disulfide (8b)——**1b** (897 mg) was added to NaSH–EtOH (prepared from 70 mg Na in 15 ml EtOH saturated with H_2S) and the mixture was stirred

16) All melting points were measured in capillary tubes and were uncorrected. NMR spectra were measured by a HITACHI R-20 60 MC and HITACHI R-22 90 MC spectrophotometer, using tetramethylsilane as the internal reference. IR and UV spectra were measured on a JASCO IRA-I grating infrared spectrophotometer and on a HITACHI EPS-3 UV spectrometer respectively.

at room temperature to separate crystals. After stirring overnight, crystals were collected by filtration and recrystallized from EtOH–H_2O to yield 495 mg (65%) of **7b**, mp 76—78°. IR ν_{max}^{KBr} cm^{-1}: 1483, 1443, 1350, 1269, 1214, 1055. UV λ_{max}^{MeOH} nm: 225 sh, 321.5. NMR (in $CDCl_3$) δ: 1.28 (t, 1H), 2.76 (m, 2H), 4.24 (m, 2H), 6.44 (s, 1H), 7.2—7.6 (m, 5H). *Anal.* Calcd. for $C_{11}H_{11}NS_3$: C, 52.17; H, 4.31; N, 5.53. Found: C, 52.09; H, 4.31; N, 5.65.

The filtrate was evaporated and the residue was taken up in H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was dried and evaporated to furnish a solid which crystallized from MeOH. **8b**, 80 mg (10.5%), mp 169—169.5. IR ν_{max}^{KBr} cm^{-1}: 1485, 1350. UV λ_{max}^{MeOH} nm: 321.5. NMR (in $CDCl_3$) δ: 2.68 (m, 4H), 4.31 (m, 4H), 6.43 (s, 2H), 7.3—7.6 (m, 10H). *Anal.* Calcd. for $C_{22}H_{20}N_2S_6$; C, 52.35; H, 3.99; N, 5.55. Found: C, 52.30; H, 4.05; N, 5.46.

Methylation of 7b——Into a methanolic suspension of **7b** (240 mg) there were added K_2CO_3 (69 mg) and CH_3I (142 mg). After stirring for 1 hr CH_3I (142 mg) was added once again and the reaction mixture was stirred for another 2 hr, evaporated, taken up in H_2O, and extracted with $CHCl_3$. The $CHCl_3$ layer was condensed, followed by chromatographing on SiO_2 with $CHCl_3$ containing 3% MeOH as solvent to give 130 mg of **10b** as a viscous syrup. NMR (in CCl_4) δ: 2.35 (s, 3H), 2.50 (double d, 2H), 3.76 (double d, 2H), 5.87 (s, 1H), 7.35 (s, 5H). *Anal.* Calcd. for $C_{12}H_{13}NS_3$: C, 53.93; H, 4.90; N, 5.24. Found: C, 53.73; H, 4.90; N, 4.96.

5-Acetyl-3-(2-mercaptoethyl)-4-methyl-4-thiazolin-2-thione (7c)——Compound **1c** was added to NaSH–EtOH (1 eq.) and stirred for 2 hr at room temperature. After evaporation, the residue was taken up in H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was dried and evaporated to give crude crystals (1.024 g) which were recrystallized from benzene to furnish yellow prisms of **7c**, 810 mg (69.3%), mp 101—101.5°. IR ν_{max}^{KBr} cm^{-1}: 1618, 1550, 1460. UV λ_{max}^{MeOH} nm (log ε): 353.4 (4.25), 292.5 (3.89), 226.9 (3.87). UV $\lambda_{max}^{5\%KOH}$ nm (log ε): 355 (4.21), 286.9 (3.74). NMR (in $CDCl_3$) δ: 1.46 (t, 1H), 2.33 (s, 3H), 2.70 (s, 3H), 2.97 (m, 2H), 4.30 (m, 2H). *Anal.* Calcd. for $C_8H_{11}ONS_3$: C, 41.20; H, 4.76; N, 6.01. Found: C, 41.47; H, 4.84, N. 6.11.

Methylation of 7c——To a suspension of **7c** (699 mg) in MeOH (10 ml) there was added CH_3I (425 mg) and K_2CO_3 (207 mg). After stirring for 17 hr, the resulted crystals were filtered and recrystallized from EtOH–H_2O to yield needles of **10c**, 440 mg (59.2%), mp 67—67.5°. IR ν_{max}^{KBr} cm^{-1}: 1627, 1560, 1430, 1302, 1150, 972. UV λ_{max}^{MeOH} nm (log ε): 353 (4.25). NMR (in $CDCl_3$) δ: 2.52 (s, 3H), 2.43 (s, 3H), 2.77 (s, 3H), 2.91 (m, 2H), 4.41 (m, 2H). *Anal.* Calcd. for $C_9H_{13}ONS_3$: C, 43.73; H, 5.30; N, 5.67. Found: C, 43.56; H, 5.33; N, 5.58.

Methylation of 7a——Methyl iodide (156 mg) and K_2CO_3 (76 mg) were added with stirring to an ethanolic solution of **7a** (210 mg). After 2 hr the solvent was evaporated and the residue was extracted with $CHCl_3$, dried, and evaporated to furnish viscous oil (230 mg) which was purified by chromatography on SiO_2 to yield 198 mg of **10a** as a syrup. IR ν_{max}^{KBr} cm^{-1}: 2895, 1592, 1439, 1373, 1324, 1281, 1163. NMR (in CCl_4) δ: 2.15 (s, 3H), 2.37 (d, 3H), 2.87 (double d, 2H), 4.28 (double d, 2H), 6.15 (q, 1H). *Anal.* Calcd. for $C_7H_{11}NS_3$: C, 40.98; H, 5.40; N, 6.83. Found: C, 40.43; H, 5.16; N, 6.93.

Reaction of 10c with CH_3I——Methyl iodide (300 mg) was added to an ethanolic solution of **10c** and the solution was heated under reflux for 2 hr. After evaporation the residue was crystallized from EtOH–H_2O to afford 120 mg of (**1a**; X=I), 89%, mp 220—221 (decomp.). *Anal.* Calcd. for $C_8H_{10}ONS_2I$: C, 29.37; H, 3.08; N, 4.59. Found: C, 29.26; H, 3.25; N, 4.55.

Oxidation of 7c——Into a solution of **7c** (200 mg) in hot EtOH, 10% H_2O_2 (2 ml) was added dropwise and allowed to stand at room temperature for 1 hr to deposit crystals, which, after standing for 3 hr, were collected by filtration. Recrystallization from benzene–*n*-hexane afforded 70 mg of **8c**, mp 117.5—119.5°. *Anal.* Calcd. for $C_{16}H_{20}O_2N_2S_6$: C, 41.14; H, 4.34; N, 6.05. Found: C, 41.14; H, 4.36; N, 6.13.

2-(4-Methylthiazolin-2-thion-3-yl)ethyl N,N-Dimethyldithiocarbamate (12a)——Dimethylammonium N,N-dimethyldithiocarbamate (500 mg) was added to a methanolic solution of **1a** (714 mg). The solution was stirred for 4 hr to separate white powder. After stirring for another 4 hr, the powder was filtered to give 110 mg of crude **12a**, mp 118—128°. The filtrate was condensed and extracted with $CHCl_3$. The $CHCl_3$ layer was dried and evaporated to give a white mass (430 mg), which was combined with the powder and crystallized from MeOH to afford 480 mg of **12a**, (57.7%), mp 129—130°. IR ν_{max}^{KBr} cm^{-1}: 1574, 1486, 1371, 1357, 1320, 1165, 1147, 963, 724. UV λ_{max}^{MeOH} nm (log ε): 243 (4.03), 277 (4.01), 321.5 (4.10). NMR (in $CDCl_3$) δ: 2.44 (d, 3H), 3.47 (d, 6H), 3.71 (m, 2H), 4.42 (m, 2H), 6.20 (q, 1H). *Anal.* Calcd. for $C_9H_{14}N_2S_4$: C, 38.85; H, 5.07; N, 10.07. Found: C, 38.79; H, 4.99; N, 10.14.

Methylation of 12a——To a suspension of **12a** (90 mg) in MeOH was added excess of CH_3I and the mixture was stirred overnight to dissolve completely. After evaporation the residue was crystallized from EtOH–ether to yield crystals of **15a**, 95 mg, mp 133—142° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 1590, 1507, 1380, 1244, 1168, 1140, 969. UV λ_{max}^{MeOH} nm (log ε): 218.8 (4.40), 243 sh (3.95), 283.5 (4.08), 298 sh (4.02). NMR (in DMSO-d_6) δ: 2.62 (d, 3H), 3.03 (s, 3H), 3.44 (d, 6H), 3.79 (m, 2H), 3.57 (m, 2H), 7.77 (q, 1H). *Anal.* Calcd. for $C_{10}H_{17}N_2S_4I$: C, 28.57; H, 4.07; N, 6.66. Found: C, 28.38; H, 4.07; N, 6.40.

2-(4-Phenylthiazolin-2-thion-3-yl)ethyl N,N-Dimethyldithiocarbamate (12b)——Dimethylammonium N,N-dimethyldithiocarbamate (566 mg) and **1a** (900 mg) were dissolved in MeOH (15 ml). After stirring overnight the resulted crystals were collected by filtration (430 mg). The filtrate was condensed to yield crystals (290 mg). The combined crystals were recrystallized from MeOH to furnish 670 mg (67%) of **12b**,

mp 128°. IR ν_{max}^{KBr} cm^{-1}: 1478, 1361, 1158, 1146, 972, 746. UV λ_{max}^{MeOH} nm (log ε): 235.0 (4.15), 278.8 (4.09), 322.2 (4.12). NMR (in $CDCl_3$) δ: 3.33 (broad s, 6H), 3.59 (double d, 2H), 4.48 (double d, 2H), 6.93 (s, 1H), 7.43 (broad s, 5H). *Anal.* Calcd. for $C_{14}H_{16}N_2S_4$: C, 49.41; H, 4.74; N, 8.23. Found: C, 49.58; H, 4.75; N, 8.25.

Methylation of 12b——Into a methanolic suspension of **12b** (150 mg) there was added excess of CH_3I. After stirring for a while the mixture became a clear solution, the solvent was evaporated and the residual white solid was crystallized from EtOH to leave white crystals of **15b**, 135 mg, mp 135—137° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 1490, 1381, 1248, 1163, 970. UV λ_{max}^{MeOH} nm (log ε): 216 (4.59), 243 sh (4.19), 283.5 (4.11), 300 sh (4.05). NMR (in DMSO-d_6) δ: 3.11 (s, 3H), 3.30 (d, 6H), 3.57 (m, 2H), 4.59 (m, 2H), 7.58 (s, 5H), 8.08 (s, 1H). *Anal.* Calcd. for $C_{15}H_{19}N_2S_4I$: C, 37.34; H, 3.94; N, 5.81. Found: C, 37.41; H, 4.19; N, 6.04.

2-(5-Acetyl-4-methylthiazolin-2-thion-3-yl)ethyl N,N-Dimethyldithiocarbamate (12c)——Dimethylammonium N,N-dimethyldithiocarbamate (498 mg) were dissolved in MeOH and the solution was stirred for 1 hr to deposit yellow precipitation, which was collected by filtration after stirring for 4 hr (260 mg, mp 170—171°). The filtrate was condensed to a half volume and left to stand to give precipitation (200 mg). The combined precipitation was crystallized from MeOH to leave orange-yellow prisms of **12c** (43.5%), mp 171—173°. IR ν_{max}^{KBr} cm^{-1}: 1636, 1571, 1502, 1367, 1310. UV λ_{max}^{MeOH} nm (log ε): 220 (4.22), 242 (4.10), 278.5 (4.09), 353.5 (4.24). NMR (in $CDCl_3$) δ: 2.37 (s, 3H), 2.82 (s, 3H), 3.46 (d, 6H), 3.68 (m, 2H), 4.48 (m, 2H). *Anal.* Calcd. for $C_{11}H_{16}ON_2S_4$: C, 41.25; H, 5.04; N, 8.75. Found: C, 41.28; H, 5.03; N, 8.77.

Methylation of 12c——Excess of CH_3I was added to a methanolic suspension of **12c** (100 mg) and the solution was stirred at 45° for 4 hr. After evaporation, the residue was crystallized from EtOH–ether to afford pale yellow crystals of **15c**, 110 mg, mp 79—81°. IR ν_{max}^{KBr} cm^{-1}: 1664, 1370, 1308, 1265. UV λ_{max}^{MeOH} nm (log ε) 219.6 (4.44), 241 sh (4.11), 276.5 (4.06), 315,0 (3.93). NMR (in DMSO-d_6) δ: 2.68 (s, 3H), 2.91 (s, 3H), 3.10 (s, 3H), 3.38 (d, 6H), 3.79 (m, 2H), 4.65 (m, 2H). *Anal.* Calcd. for $C_{12}H_{19}ON_2S_4I$: C, 31.02; H, 4.14; N, 6.06. Found: C, 30.94; H, 4.33, N, 6.41.

Alkaline Hydrolysis of 12b——To a suspension of **12b** (500 mg) in ethylene glycol (10 ml) was added aqueous KOH (150 mg in 1 ml). The mixture was heated at 120—150° in an oil bath for 1 hr to give a white emulsion. After cooling, the mixture was acidified at pH 4 to smell strongly like hydrogensulfide and deposited traces of powder. The powder was filtered off and the filtrate was concentrated. The residue was crystallized from benzene–*n*-hexane to furnish prisms of 2-mercapto-4-phenylthiazole (**14**), 250 mg (89%), mp 165—167°. Optical properties of **14** are in good agreement with those reported.[17]

Alkaline Hydrolysis of 15b——To a methanolic suspension of **15b** (120 mg) were added 3 drops of 10% KOH to smell strong odor of methylmercaptan. After standing for 30 min, the solvent was evaporated and the residue was taken up in H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was evaporated to give 80 mg of white solid which was crystallized from benzene–*n*-hexane to yield 50 mg of **16b**, mp 121.5—122°. IR ν_{max}^{KBr} cm^{-1}: 1655 sh, 1645, 1492, 1383, 1272, 968. UV λ_{max}^{MeOH} nm (log ε): 217 sh (4.26), 246.2 (4.14), 274.5 (4.12). NMR (in $CDCl_3$) δ: 3.20—3.65 (8H), 4.04 (m, 2H), 5.97 (s, 1H), 7.42 (s, 5H). *Anal.* Calcd. for $C_{14}H_{16}ON_2S_3$: C, 51.85; H, 4.97; N, 8.64. Found: C, 52.03; H, 4.96; N, 8.81.

Reaction of 15b with Benzylamine——Benzylamine (72 mg) was added to a methanolic suspension of **15b** (160 mg) with stirring to dissolve gradually with the evolution of the odor of methylmercaptan. After stirring for 1 hr, the solvent was evaporated and the residue was extracted with $CHCl_3$. The extracts were dried, evaporated, and chromatographed on SiO_2 with $CHCl_3$ containing 1% MeOH to afford crystals. Recrystallization from MeOH gave 60 mg of **17b**, mp 90.5—91°. IR ν_{max}^{KBr} cm^{-1}: 1621, 1604, 1492, 1376, 1354, 1130, 743. UV λ_{max}^{MeOH} nm (log ε): 216 sh (4.42), 249.5 (4.24), 260 sh (4.23) 267 sh (4.25), 272.5 (4.26). $\lambda_{max}^{H^+}$ nm (log ε): 252 sh (4.25), 268.3 (4.29). NMR (in $CDCl_3$) δ: 3.15—3.45 (broad d, 6H), 3.59 (m, 2H), 4.12 (m, 2H), 4.38 (s, 2H), 5.74 (s, 1H), 7.35 (m, 5H), 7.39 (s, 5H). *Anal.* Calcd. for $C_{21}H_{23}N_3S_3$: C, 61.01; H, 5.61; N, 10.16. Found: C, 60.95; H, 5.33; N, 10.21.

Reaction of 1b with Sodium Thiophenolate——Thiophenol (484 mg) and Na (192 mg) were dissolved in abs. MeOH (25 ml), and **1b** (1200 mg) was added and the mixture was heated under reflux for 1 hr. After evaporation the residue was taken up in H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was dried and evaporated to give a yellow mass. Recrystallization from MeOH afforded white needles of **18b**, 335 mg, mp 120—121°. IR ν_{max}^{KBr} cm^{-1}: 1583, 1484, 1439, 1370, 1278. UV λ_{max}^{MeOH} nm (log ε) 252.0 (3.97), 322.5 (4.41). NMR (in $CDCl_3$) δ: 3.15 (m, 2H), 4.35 (m, 2H), 6.43 (s, 1H), 7.12 (s, 5H), 7.3—7.6 (m, 5H). *Anal.* Calcd. for $C_{17}H_{15}NS_3$: C, 62.00; H, 4.59; N, 4.25. Found: C, 61.77; H, 4.83; N, 4.32.

The mother liquor was shown by thin-layer chromatography to consist of five species and separated by chromatography on SiO_2 with $CHCl_3$. The first oily fraction (14 mg) was purified by rechromatography on SiO_2 with benzene–*n*-hexane (1: 1) to yield 4 mg of **23** as a syrup. UV λ_{max}^{MeOH} nm: 240.5, 256 sh. NMR (in $CDCl_3$) δ: 2.41 (s, 4H), 7.12 (s, 10H). Mass Spectrum *m/e*: 278, 109, 77.

The second crystalline fraction was recrystallized from MeOH to leave 85 mg of **18b**, mp 118° (sums-total 420 mg, 32%).

17) F.B. Dains and O.A. Krober, *J. Am. Chem. Soc.*, **61**, 1830 (1939).

Rechromatography of the third syrupy fraction (240 mg), which was shown by thin-layer chromatography to consist of two species, on SiO_2 with benzene gave initially 127 mg of **21** as a viscous oil which crystallized from *n*-hexane to furnish 110 mg of **21** (17%), mp 49—49.5° (lit.[18] mp 52°). IR ν_{max}^{KBr} cm^{-1}: 1475, 1444, 1415, 1303. NMR (in $CDCl_3$) δ: 7.28—7.49 (m, 4H), 7.80—7.97 (m, 2H), 8.81 (d, 1H).

Elution of the third fraction on rechromatography with benzene gave secondarily 109 mg of **22** which was recrystallized from MeOH to leave disulfide (**22**), 100 mg (6.2%), mp 55.5—58°. IR ν_{max}^{KBr} cm^{-1}: 1660, 1442, 1260, 780, 719. UV λ_{max}^{MeOH} nm (log ε): 255 (4.13). NMR (in CCl_4) δ: 2.4—3.2 (m, 6H), 3.88 (double d, 2H), 5.90 (s, 1H), 7.23 (s, 5H), 7.35 (s, 5H). Mass Spectrum *m/e*: 405, 296, 236, 204, 176, 169, 141, 134. *Anal.* Calcd. for $C_{19}H_{19}ONS_4$: C, 56.29; H, 4.72; N, 3.46; S, 31.64. Found: C, 56.29; H, 4.73; N, 3.40; S, 31.85.

The final crystalline fraction eluted with $CHCl_3$ was recrystallized from benzene–*n*-hexane to furnish 110 mg of **6b** (11.6%), mp 112—113°.

Reaction of 1a with Sodium Thiophenolate——Thiophenol (440 mg) and Na (92 mg) were dissolved in abs. MeOH, **1a** (1.13 g) was added, and the solution was heated under reflux with stirring for 30 min. After cooling the solvent was removed and the residue was taken up in $CHCl_3$, washed with water, and dried and the solvent was removed to yield a crude mixture (1.2 g). This was chromatographed on SiO_2 with $CHCl_3$ containing 1% MeOH. A compound (156 mg) was isolated from the earlier fractions (5—7). Crystallization from MeOH gave pure diphenyldisulfide (75 mg), mp 55—57° (lit.[19] mp 62.5—63.5°). Fractions (10—16) (300 mg) were rechromatographed to give 237 mg of **18a** as a viscous syrup (22.3%). This was methylated without further purification. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1586, 1441, 1369, 1321, 1275, 980. UV λ_{max}^{MeOH} nm: 252.5, 321.5. NMR (in $CDCl_3$) δ: 2.17 (d, 3H), 3.38 (double d, 2H), 4.33 (double d, 2H), 6.12 (q, 1H), 7.1—7.6 (m. 5H).

Finally, the later fractions (43—46) gave red syrup (220 mg), which slowly crystallized from MeOH to afford **6a**, 75 mg, mp 81°.

Methylation of 18a——Compound **18a** (170 mg) and CH_3I (100 mg) was dissolved in a mixture of MeOH (5 ml) and $CHCl_3$ (5 ml), and the solution was stirred for 2.5 hr. After evaporation the crystalline residue was recrystallized from EtOH–ether to furnish crystals of **19a**, 180 mg, mp 118—125° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 3010, 1582, 1482, 1468, 1319, 1160. UV λ_{max}^{MeOH} nm (log ε) 217.8 (4.34), 250.0 (3.80), 296.7 (3.96). NMR (in DMSO-d_6) δ: 2.51 (s, 3H), 2.93 (s, 3H), 3.53 (double d, 2H), 4.46 (double d, 2H), 7.35 (5H), 7.77 (s, 1H). *Anal.* Calcd. for $C_{13}H_{16}NS_3I$: C, 38.11; H, 3.94; N, 3.45. Found: C, 37.89; H, 3.88; N, 3.58.

Reaction of 1c with Sodium Thiophenolate——Thiophenol (440 mg) and Na (95 mg) were dissolved in abs. MeOH (20 ml), **1c** (886 mg) was added, and the mixture was heated under reflux for 30 min. After evaporation the residue was taken up in $CHCl_3$, washed with water, and dried and the solvent was removed to afford red syrup (990 mg). This was chromatographed on SiO_2 with $CHCl_3$ containing 0.5% MeOH. The first crystalline fraction was recrystallized from MeOH to leave white needles of **18c**, 340 mg (27.6%), mp 78.5—80°. IR ν_{max}^{KBr} cm^{-1}: 1665, 1550, 1357, 1283, 1152, 747. UV λ_{max}^{MeOH} nm (log ε) 252.7 (3.89), 295 (3.59), 353.5 (4.21). NMR (in $CDCl_3$) δ: 2,29 (s, 3H), 2.56 (s, 3H), 3.35 (double d, 2H), 3.49 (double d, 2H), 7.10—7.55 (5H). *Anal.* Calcd. for $C_{14}H_{15}ONS_3$: C, 54.37; H, 4.89; N, 4.53. Found: C, 54.63; H, 4.86; N, 4.69. The second crystalline fraction was recrystallized from EtOH to furnish 225 mg of **6c** (25.8%), mp 149—149.5°.

Methylation of 18b——Excess of CH_3I and **18b** (340 mg) were dissolved in MeOH. After stirring for 2 hr, the solvent was evaporated and the crystalline residue was recrystallized from EtOH–ether to yield **19b**, 355 mg (73%) as pale yellow scales, mp 107—110° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 1566, 1486, 1441, 1415, 1155. UV λ_{max}^{MeOH} nm (log ε): 214 sh (4.49), 247 sh (4.02), 297.5 (4.01). NMR (in DMSO-d_6) δ: 3.07 (s, 3H), 3.19 (m, 2H), 4.39 (m, 2H), 7.0—7.4 (m, 5H), 7.55 (s, 5H), 8.04 (s, 1H). *Anal.* Calcd. for $C_{18}H_{18}NS_3I$: C, 45.85; H, 3.85; N, 2.99. Found: C, 46.04; H, 3.83; N, 3.23.

Methylation of 18c——Excess of CH_3I and **18c** (100 mg) were added to MeOH and the mixture was stirred till the compound was dissolved completely. After stirring for another hour, the solvent was evaporated to give syrup. Recrystallization twice from MeOH–ether gave 80 mg of **19c**, mp 116—117° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 1695, 1570, 1395, 1280, 1270. UV λ_{max}^{MeOH} nm (log ε): 218.5 (4.40), 251.4 (3.90), 308.5 (4.06). NMR (in DMSO-d_6) δ: 2.62 (s, 3H), 2.80 (s, 3H), 3.05 (s, 3H), 3.58 (double d, 2H), 4.61 (double d, 2H). *Anal.* Calcd. for $C_{15}H_{18}ONS_3I$: C, 39.69; H, 4.02; N, 3.10. Found: C, 39.54; H, 4.15; N, 3.27.

Alkaline Hydrolysis of 19b——Into a stirred solution of **19b** (100 mg) in MeOH (6 ml) there was added 4 drops of 10% KOH. After stirring for 20 min, the separated crystals were collected by filtration. The filtrate was evaporated and the residue was extracted with $CHCl_3$. The $CHCl_3$ layer was evaporated and the residue was combined with crystals. Recrystallization from EtOH–H_2O furnished 50 mg of **20**, mp 107—108°. IR ν_{max}^{KBr} cm^{-1}: 1660, 1582, 1483, 1440. UV λ_{max}^{MeOH} nm (log ε): 252.8 (4.11), 280 sh (3.63). *Anal.* Calcd. for $C_{17}H_{15}ONS_2$: C, 65.17; H, 4.82; N, 4.47. Found: C, 65.31; H, 4.67; N, 4.70.

Reaction of 19b with NaSH——One hundr ed mg of **19b** was suspended in abs. EtOH and treated with NaSH. After stirring for 2 hr, the resulted solution was evaporated, taken up in $CHCl_3$, washed with H_2O,

18) M. Wohmann, *Ann.*, **259**, 277 (1880).
19) E.E. Campaigne, J. Tsurugi, and W.W. Mayer, *J. Org. Chem.*, **26**, 2486 (1961).

and dried and the solvent was evaporated. The residue was crystallized from MeOH to afford 40 mg of **18b**.

Reaction of 1 with NH_4SCN——To a methanolic suspension or solution of **1** there was added NH_4SCN, and the mixture was stirred to deposit crystals, which were filtered and recrystallized from EtOH to yield thiocyanate salt of **1** in quantitative yield. (**1b**: X=SCN), mp 130—132°. *Anal.* Calcd. for $C_{12}H_{10}N_2S_3$: C, 51.80; H, 3.62; N, 10.07. Found: C, 51.77; H, 3.89; N, 10.07. (**1a**: X=SCN), white prisms, mp 104—106°. *Anal.* Calcd. for $C_7H_8N_2S_3$: C, 38.89; H, 3.73; N, 12.96. Found: C, 38.89; H, 3.78; N, 13.01. (**1d**: X=SCN), white prisms, mp 177—180°. *Anal.* Calcd. for $C_{10}H_{12}O_2N_2S_3$: C, 41.67; H, 4.20; N, 9.72. Found: C, 41.56; H, 4.02; N, 10.09.

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