Chem. Pharm. Bull.
22(3) 505—513 (1974)

UDC 547.496.1.04 : 547.339.2.04 : 547.9.02

Studies on Fungicides. XXV.[1] Addition Reaction of Dithiocarbamates to Fumaronitrile, Bis(alkylthio)maleonitrile, 2,3-Dicyano-5,6-dihydro-1,4-dithiin and 4,5-Dicyano-2-oxo-1,4-dithiole

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(Received April 28, 1973)

5-Cyanomethyl-2-thioxo-4-aminothiazolines (II) were prepared by the addition reaction of dithiocarbamates to fumaronitrile. In the reactions of bis(methylthio)maleonitrile (IXa), bis(benzylthio)maleonitrile (IXb), 2,3-dicyano-5,6-dihydro-1,4-dithiin (IXc) and 4,5-dicyano-2-oxo-1,4-dithiole (IXd) with dithiocarbamates were obtained 5,5′-bi-2-thioxo-4-aminothiazolines (X). The 4-amino groups of II and X were found to be labile and were hydrolyzed when heated with mineral acids to give 5-cyanomethyl-2-thioxo-4-thiazolidones (III) and 5,5′-bi-2-thioxo-4-thiazolidones (XII), respectively. X was also found to be converted to $\Delta^{5,5'}$-bi-2-thioxo-4-iminothiazolidine (XI) by autoxidation in the presence of catalytic amount of triethylamine. 4-Oxo-4′-imino-$\Delta^{5,5'}$-bi-2-thioxo-thiazolidine (XVI) was prepared by the addition reaction of N-benzyldithiocarbamate to 5-cyanomethylidene-2-thioxo-4-thiazolidone (XIV). XI and XIV gave $\Delta^{5,5'}$-bi-2-thioxo-4-thiazolidones (XIII) on hydrolysis with mineral acids.

In an extention of the investigation on the addition reactions of dithiocarbamates to activated double bonds[3] this paper further describes the reactions of dithiocarbamates with fumaronitrile (I), bis(alkylthio)maleonitrile (IXa, b), 2,3-dicyano-5,6-dihydro-1,4-dithiin (IXc) and 4,5-dicyano-2-oxo-1,3-dithiole (IXd). I and IXa, b, c, d are readily accessible from fumaramide[4] and bis(mercapto)maleonitrile,[5] respectively.

The double bonds of these compounds are activated by cyano groups and are expected to react readily with nucleophiles. Thus I and IXa, b, c, d were reacted with dithiocarbamates. In the reaction of dithiocarbamates with IXa, b, c, d the eliminations of the thiol residues caused the formation of the compounds (X).

Addition Reaction of Dithiocarbamates to Fumaronitrile

Fumaronitrile (I) was found to react with triethylammonium dithiocarbamates on heating in acetone to give the moderately stable 1: 1 adducts (II). The infrared (IR) spectra of the adducts show the absorptions at 3400—3200 (NH_2), 2240 (CN) and 1655—1640 cm^{-1} (=C-NH_2). In the nuclear magnetic resonance (NMR) spectra appear the absorptions at δ 5.8 (NH_2) and δ 3.80—3.99 (CH_2, singlet). These data are consistent not only with the anticipated structure II but also with V and VI. However, the structures (V) and (VI) were ruled out since the adducts gave 5-methoxycarbonylmethyl-2-thioxo-4-thiazolidones (IVa, b)[3a] on treatment with hot methanolic hydrogen chloride.

5-Cyanomethyl-2-thioxo-4-aminothiazolines (II) thus obtained were found to be partially hydrolyzed with hydrochloric acid under mild conditions to give 5-cyanomethyl-2-thioxo-4-

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[1] Part XXIV: H. Nagase, *Chem. Pharm. Bull.* (Tokyo), **22**, 42 (1974).

[2] Location: *Higashiyodogawa-ku, Osaka.*

[3] *a)* J. Kinugawa and H. Nagase, *Yakugaku Zasshi*, **86**, 95, 101 (1966); *b)* H. Nagase, *Chem. Pharm. Bull.* (Tokyo), **21**, 279 (1973); *c)* H. Nagase, *ibid.*, **21**, 1132 (1973).

[4] R.T. Bertz, "Organic Syntheses," Coll. Vol. IV, ed. by N. Rabjohn, John Wiley and Sons, Inc., New York, 1963, p. 486.

[5] *a)* H.E. Simmons, D.C. Blomstrom, and R.D. Vest, *J. Am. Chem. Soc.*, **84**, 4756 (1962); *b)* E. Klingsberg, *ibid.*, **86**, 5290 (1964).

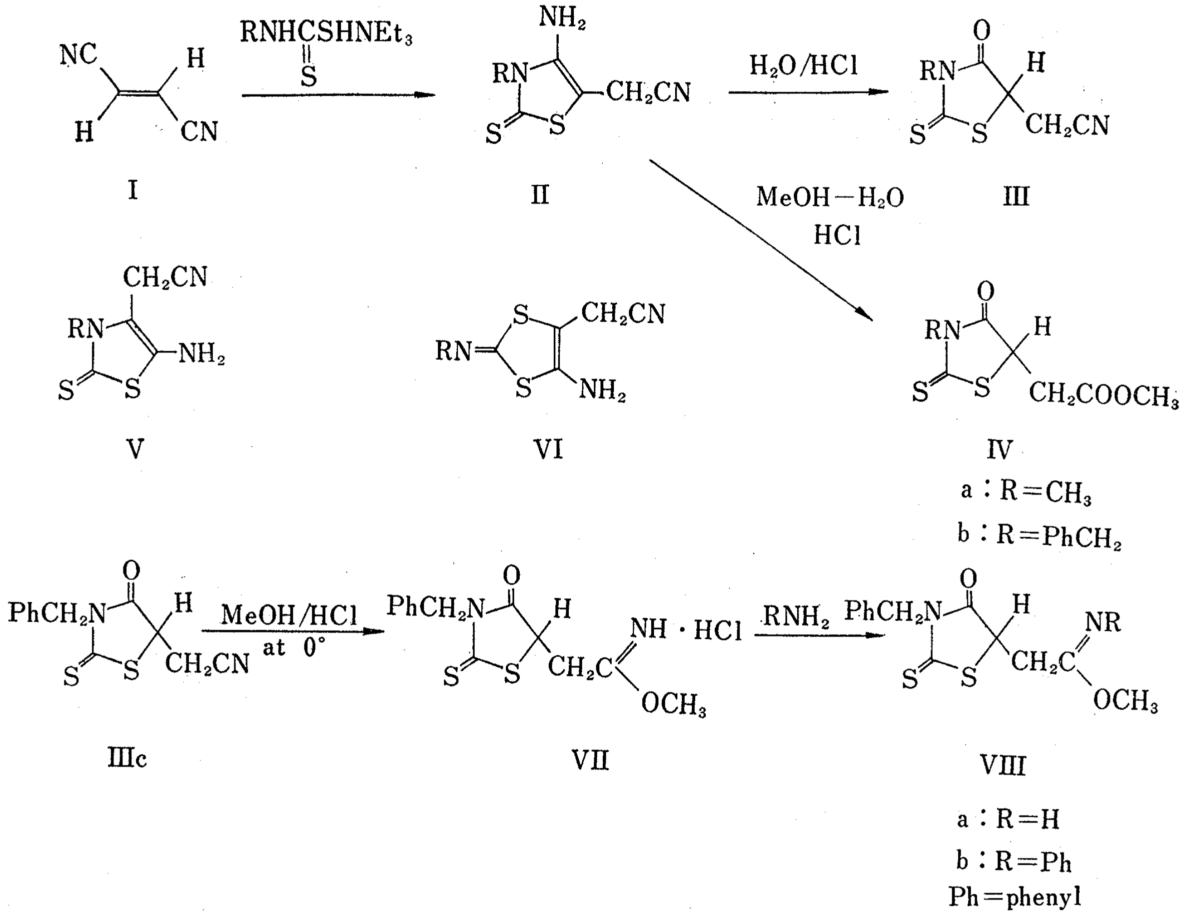

Chart 1

Table I. 5-Cyanomethyl-2-thioxo-4-aminothiazolines (II)

Compd. No.	R	mp (°C)	Appearance	Method[a] (% yield)	Formula	Analysis (%) Found (Calcd.) C	H	N
IIa	CH_3	147—148	pale brown needles	A (81.4)	$C_6H_7N_3S_2$	39.18 (38.92)	3.66 (3.81)	22.54 (22.70)
IIb	Ph[b]	170—171	pale brown leaflets	A (63.2)	$C_{11}H_9N_3S_2$	53.51 (53.44)	3.50 (3.67)	16.73 (17.00)
IIc	$PhCH_2$[b]	164—165	pale brown needles	A (96.3)	$C_{12}H_{11}N_3S_2$	55.43 (55.17)	4.17 (4.24)	16.08 (16.09)
IIb	2-Cl-$PhCH_2$[b]	182—183	light brown scales	A (95.0)	$C_{12}H_{10}N_3S_2Cl$	48.98 (48.72)	3.42 (3.41)	14.06 (14.21)
IIe	4-Cl-$PhCH_2$[b]	149—150	pale brown needles	A (89.7)	$C_{12}H_{10}N_3S_2Cl$	48.51 (48.72)	3.26 (3.41)	14.03 (14.21)
IIf	2,4-Cl_2-$PhCH_2$[b]	154—155	pale brown powder	A (92.9)	$C_{12}H_9N_3S_2Cl_2$	43.83 (43.64)	2.62 (2.75)	12.43 (12.72)
IIg	2,6-Cl_2-$PhCH_2$[b]	174—175	brown scales	A (96.1)	$C_{12}H_9N_3S_2Cl_2$	43.88 (43.64)	2.64 (2.75)	12.32 (12.72)

[a] See the experimental section.
[b] Ph=phenyl

thiazolidones (III) as was observed with 5-phenyl-2-thioxo-4-aminothiazolines.[6] The structure of III was assigned with spectral data. The ultraviolet (UV) spectra of III show the

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6) E.C. Taylor, Jr., J. Wolinsky, and H.H. Lee, *J. Am. Chem. Soc.*, **76**, 1870 (1954).

Table II. Spectral Data of II

Compd. No.	IR Spectra $\nu_{\max}^{\text{Nujol}}$ (cm^{-1})			NMR Spectra[a] (δ ppm) in d_6-DMSO		
	NH_2		CN	R	NH_2	CH_2
IIa	3350, 3270 3220	1655	2240	3.55(s)	5.85 (broad)	3.92(s)
IIb	3440, 3290 3200	1640	2240	7.20—7.70(m)	5.33 (broad)	3.95(s)
IIc	3380, 3330 3250, 3220	1645	2240	5.46(s) 7.27(s)	5.76 (broad)	3.88(s)
IId	3380, 3260 3190	1645	2240	5.48(s) 6.45—6.72(m) 7.20—7.60(m)	5.87 (broad)	3.97(s)
IIe	3400, 3320 3230	1645	2240	5.45(s) 7.38(s)	5.81 (broad)	3.81(s)
IIf	3380, 3300 3260	1645	2240	5.45(s) 6.55, 6.68 7.30—7.75(m)	5.87 (broad)	3.99(s)
IIg	3380, 3300 3250, 3220	1645	2240	5.48(s) 7.36(s)	5.82 (broad)	3.94(s)

[a] s: singlet; m: multiplet

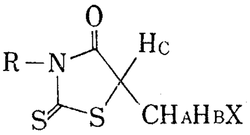
characteristic absorptions of 2-thioxo-4-thiazolidones in the region of 260 nm and 295 nm. The IR spectra of III reveal the absorptions at 2250 and in the region of 1720—1735 cm^{-1} reasonably assigned to the cyano and carbonyl groups, respectively. In the NMR spectra of III the absorptions of the annular methyne protons appear at δ 4.36—5.16 as triplets and those of the methylene protons appear at δ 3.00—3.46 as doublets.

Table III. 5-Cyanomethyl-2-thioxo-4-thiazolidones (III)

Compd. No.	R	mp (°C)	Appearance (Recrystn. solvent)	Method[a] (% yield)	Formula	Analysis (%) Found (Calcd.)		
						C	H	N
IIIa	CH_3	74— 75	pale brown needles (EtOH)	B (80.0)	$C_6H_6ON_2S_2$	38.90 (38.72)	3.02 (3.25)	15.11 (15.05)
IIIb	Ph[b]	107—109	pale brown needles (EtOH)	B (69.3)	$C_{11}H_8ON_2S_2$	53.10 (53.28)	3.13 (3.25)	11.03 (11.29)
IIIc	$PhCH_2$[b]	115—116	colorless needles (EtOH)	B (85.0)	$C_{12}H_{10}ON_2S_2$	54.93 (54.96)	3.67 (3.84)	10.76 (10.68)
IIId	2-Cl-$PhCH_2$[b]	133—135	colorless needless (EtOH)	B (90.0)	$C_{12}H_9ON_2S_2$	48.76 (48.56)	3.00 (3.06)	9.36 (9.44)
IIIe	4-Cl-$PhCH_2$[b]	129—130	colorless needles (EtOH)	B (86.0)	$C_{12}H_9ON_2S_2$	48.24 (48.56)	2.95 (3.06)	9.70 (9.44)
IIIf	2,4-Cl_2-$PhCH_2$[b]	130—131	colorless scales (EtOH)	B (83.5)	$C_{12}H_8ON_2S_2$	43.38 (43.51)	2.40 (2.43)	8.51 (8.46)
IIIg	2,6-Cl_2-$PhCH_2$[b]	153—154	colorless needles (EtOH)	B (72.7)	$C_{12}H_8ON_2S_2$	43.43 (43.51)	2.17 (2.43)	8.48 (8.46)

[a] See the experimental section.
[b] Ph=phenyl

TABLE IV. Spectral Data of



Compd. No.	R	X	NMR spectra (δ ppm)[a) J (Hz)			IR spectra ν_{max}^{Nujol} (cm^{-1})		UV spectra λ_{max}^{EtOH} (nm) (log ε)	
			H_A, H_B	H_C	Solvent	C=O	CN		
IIIa	CH_3	CN	3.15(d)	4.50(t) J =6.0	$CDCl_3$	1720	2250		
IIIb	Ph[b)	CN	3.14(d)	4.52(t) J =5.5	$CDCl_3$	1730	2250	258 (3.98)	295 (4.16)
IIIc	$PhCH_2$[b)	CN	3.00(d)	4.36(t) J =6.0	$CDCl_3$	1735	2240	261 (4.08)	295 (4.18)
IIId	2-Cl-$PhCH_2$[b)	CN	3.27(d)	4.76(t) J =5.5	d_6-DMSO	1735	2250	258 (4.09)	295 (4.16)
IIIe	4-Cl-$PhCH_2$[b)	CN	3.43(d)	5.06(t) J =5.5	d_6-DMSO	1725	2250	260 (4.07)	295 (4.17)
IIIf	2,4-Cl_2-$PhCH_2$[b)	CN	3.46(d)	5.10(t) J =5.5	d_6-DMSO	1735	2250		
IIIg	2,6-Cl_2-$PhCH_2$[b)	CN	3.35(d)	5.03(t) J =6.0	d_6-DMSO	1730	2250		
VIIIa	$PhCH_2$[b)	$-\underset{OCH_3}{C}=NH$	3.08, 2.84 J_{AB}=16.0 J_{AC}=8.5 J_{BC}=5.0	4.40	$CDCl_3$	1725 3300 1660	(C=O) (NH) (C=N)		
VIIIb	$PhCH_2$[b)	$-\underset{OCH_3}{C}=NPh$	3.00, 2.83 J_{AB}=16.0 J_{AC}=7.0 J_{BC}=5.5	4.31	$CDCl_3$	1748 1660	(C=O) (C=N)		

a) d: doublet; t: triplet
b) Ph=phenyl

3-Benzyl-5-cyanomethyl-2-thioxo-4-thiazolidone (IIIc) afforded 3-benzyl-5-methoxycarbonimidoylmethyl-2-thioxo-4-thiazolidone hydrochloride (VII) on treatment with cooled methanolic hydrogen chloride. VII reacted with ammonia and aniline to give VIIIa, b, respectively, whose structures were identified with spectral data (Table IV). The IR spectra of VIIIa, b show the absorptions at 1660 and in the region of 1725—1748 cm^{-1} reasonably assigned to the imino and carbonyl groups, respectively. The NMR spectra of VIIIa, b show the characteristic patterns of ABX system with approximate coupling constants of $J_{AB}=16$, $J_{AX}=7.0$—8.5 and $J_{BX}=5.0$—5.5 Hz. It should be noted that the methylene protons adjacent to an assymmetric center are expected to become magnetically nonequivalent.[7)

Similar ABX patterns were observed[8) in the NMR spectra of 2-oxo-(or imino)-4-thiazolidone-5-acetates. The large values of J_{AB}'s were referred to as "carbonyl effect" on the coupling constants for the methylene groups by Takahashi[9) in the structurally related 2-thioxo-4-thiazolidone-5-acetates.[3a) The carbonimidoyl group in VIIIa, b seems to exert influence similar to "carbonyl effect" on the coupling constants for the adjacent methylene protons.

Addition Reaction of Dithiocarbamates to Bis(alkylthio)maleonitrile (IXa, b), 2,3-Dicyano-5,6-dihydro-1,4-dithiin (IXc) and 4,5-Dicyano-2-oxo-1,3-dithiole (IXd)

IXa, b, c, d reacted with triethylammonium N-methyldithiocarbamate on heating in

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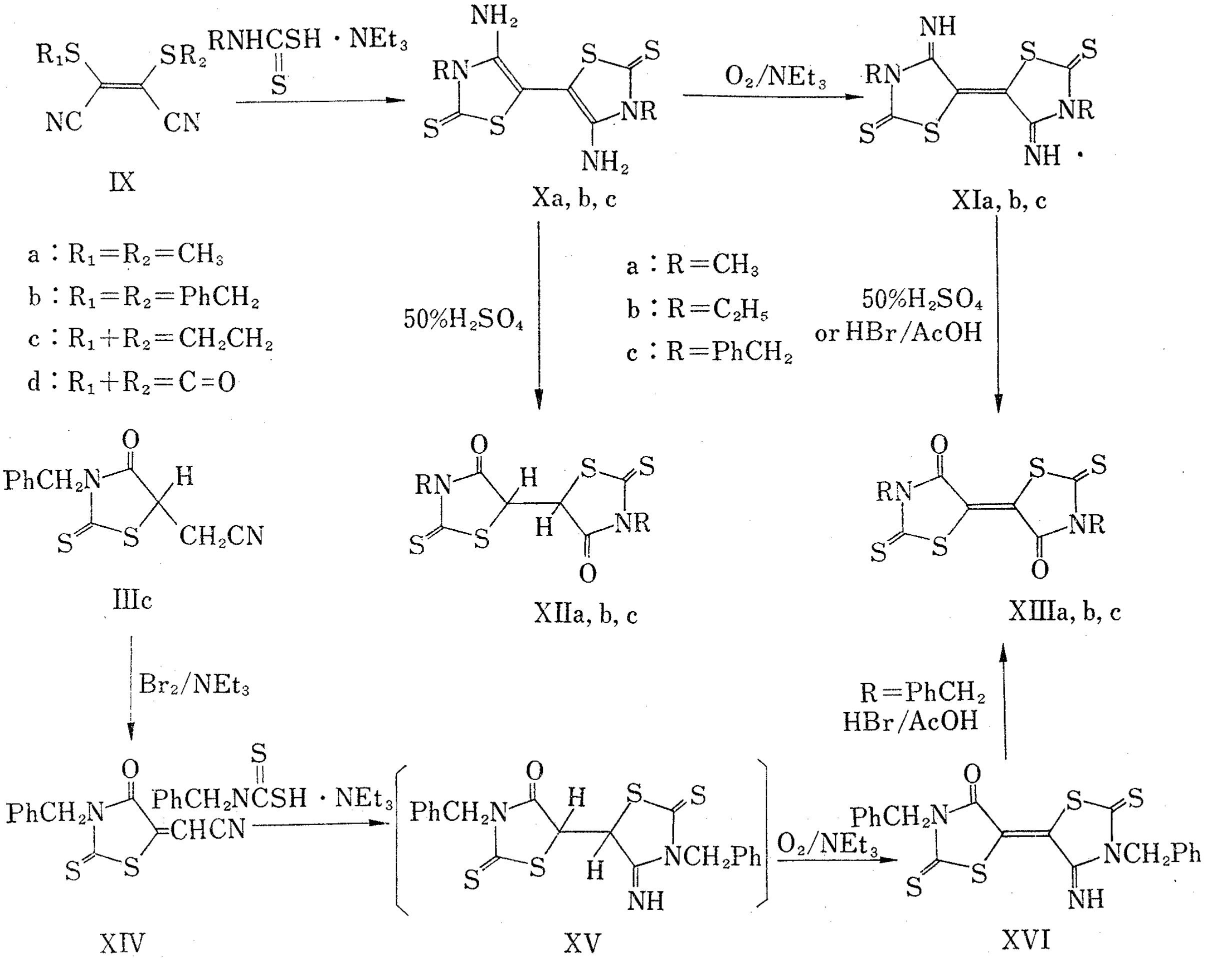
7) J.W. Emsley, J. Feeney, and L.H. Sutcliffe, "High Resolution NMR Spectroscopy," Vol. 1, Pergamon Press, 1965, p. 560.
8) H. Nagase, *Chem. Pharm. Bull.* (Tokyo), **21**, 270 (1973).
9) T. Takahashi, *Tetrahedron Letters*, **1964**, 565.

acetone or ethanol to give the same product of $C_8H_{10}N_4S_4$. This compound was obtained in good yield when one mole of IXa, b, c, d was treated with two moles of the dithiocarbamate. In the reaction of triethylammonium N-methyldithiocarbamate with IXb was isolated dibenzyldisulfide along with the product described above.

The IR spectrum of the product shows the absorptions assigned to NH_2 in the region of 3200—3430 cm^{-1} (Table VI). The UV and NMR spectra were not measured because of its poor solubilities in proper solvents. For the structural determination the product was hydrolyzed with 50% sulfuric acid and found to give the known 3,3′-dimethyl-5,5′-bi-2-thioxo-4-thiazolidone (XIIa).[3b)] The results described above indicate that the structure of the product should be 3,3′-dimethyl-5,5′-bi-2-thioxo-4-aminothiazoline (Xa). In the same manner were also obtained Xb, c, which gave XIIb, c on hydrolysis with 50% sulfuric acid.



Ph=phenyl

Chart 2

5,5′-Bi-2-thioxo-4-aminothiazolines (Xa, b, c) were found to be readily autoxidized in the presence of triethylamine into $\Delta^{5,5'}$-bi-2-thioxo-4-iminothiazolidines (XIa, b, c), respectively. It appears that triethylamine catalyses the autoxidation by the formation of carbanion at the 5-position of the thiazoline ring. The structure of XIa, b, c were identified by spectral data and hydrolysis. Thus XIa, b, c show IR absorptions assigned to C=NH in the region of 3200—3250 cm^{-1} (Table VI) and afforded the known $\Delta^{5,5'}$-bi-2-thioxo-4-thiazolidones (XIIIa, b, c)[3b,c)] on hydrolysis with 50% sulfuric acid or 30% hydrogen bromide in acetic acid. It has been already reported[3b,c)] that 5,5′-bi-2-thioxo-4-thiazolidones (XII) are readily autoxidized in the presence of triethylamine to give $\Delta^{5,5'}$-bi-2-thioxo-4-thiazolidones

TABLE V. 5,5′-Bi-2-thioxo-4-aminothiazolines (X) and $\Delta^{5,5'}$-Bi-2-thioxo-4-iminothiazolidines (XI)

Compd. No.	R	mp (°C)	Appearance (recrystan. solvent)	Method[a] (% yield)	Formula	Analysis (%) Found (Calcd.) C	H	N
Xa	CH_3	260 decomp.	yellow powder (DMF–H_2O)	C (64.5)	$C_8H_{10}N_4O_4$	33.14 (33.08)	3.52 (3.47)	19.12 (19.29)
Xb	C_2H_5	239 decomp.	yellow powder (DMF–H_2O)	C (43.7)	$C_{10}H_{14}N_4S_4$	37.83 (37.71)	4.50 (4.43)	17.59 (17.59)
Xc	$PhCH_2$[b]	270 decomp.	dark green scales (DMF)	C (58.5)	$C_{20}H_{18}N_4S_4$	54.04 (54.30)	4.02 (4.10)	12.57 (12.67)
XIa	CH_3	270 decomp.	red brown powder	D (69.6)	$C_8H_8N_4S_4$	33.37 (33.34)	2.84 (2.80)	19.21 (19.44)
XIb	C_2H_5	255 decomp.	yellow powder	D (71.3)	$C_{10}H_{12}N_4S_4$	37.75 (37.98)	3.83 (3.83)	17.55 (17.72)
XIc	$PhCH_2$[b]	275 decomp.	dark green needles	D (58.5)	$C_{20}H_{16}N_4S_4$	54.12 (54.55)	3.76 (3.66)	12.59 (12.72)

[a] See the experimental section.
[b] Ph=phenyl

TABLE VI. IR Spectral Data of 5,5′-Bi-2-thioxo-4-aminothiazolines (X) and $\Delta^{5,5'}$-Bi-2-thioxo-4-iminothiazolidines (XI)

Compd. No.		ν_{max}^{Nujol} (cm^{-1}) C=$\overset{|}{C}$–NH$_2$		C=NH, C=C
Xa	CH_3	3430(m), 3325(s), 3275(m)	1645(s), 1620(m), 1575(w)	
Xb	C_2H_5	3320(s), 3200(m), 3150(s)	1610(w), 1570(s)	
Xc	$PhCH_2$[a]	3340(m), 3275(s)	1645(m), 1625(m), 1575(m)	
XIa	CH_3			3240(s), 1635(s), 1625(s)
XIb	C_2H_5			3220(s), 1625(s)
XIc	$PhCH_2$[a]			3250(s), 1630(m), 1625(s)

s: strong; m: medium; w: weak
[a] Ph=phenyl

(XIII) and that XIII has the *trans* configuration, preferentially stabilized by intramolecular interaction (which is only possible in the *trans* configuration). It appears that XI has also *trans* configuration as shown in Chart 2. The autoxidation of X to XI was not so easy as that of XII to XIII and needed longer reaction-time.

In the reaction mixtures of the hydrolysis of X or XI partially hydrolyzed 4-oxo-4′-imino-5,5′-bi-2-thioxo-thiazolidines or 4-oxo-4′-imino-$\Delta^{5,5'}$-bi-2-thioxo-thiazolidines were not isolated. In an attempt to synthesize 3,3′-dibenzyl-4-oxo-4′-imino-5,5′-bi-2-thioxo-thiazolidine (XV) alternatively, 3-benzyl-5-cyanomethylidene-2-thioxo-4-thiazolidone (XIV), which was derived from IIIc by bromination and subsequent dehydrobromination, was treated with triethylammonium N-benzyldithiocarbamate. The product shows IR absorptions assigned to C=NH at 3300 and 1630 cm^{-1} and gave $\Delta^{5,5'}$-bi-2-thioxo-4-thiazolidones (XIIIc) when hydrolyzed with 30% hydrogen bromide in acetic acid. This implies that the initially formed 4-oxo-4′-imino-5,5′-bi-2-thioxo-thiazolidine (XV) was readily autoxidized to 4-oxo-4′-imino-$\Delta^{5,5'}$-bi-2-thioxo-thiazolidine (XVI) in the presence of triethylamine.

The formation of 5,5′-bi-2-thioxo-4-aminothiazolines (X) in the reaction of IXa, b, c, d with dithiocarbamates can be interpreted in the following manner.

IXa, b, c, d would react initially with dithiocarbamates to give the intermediate com-

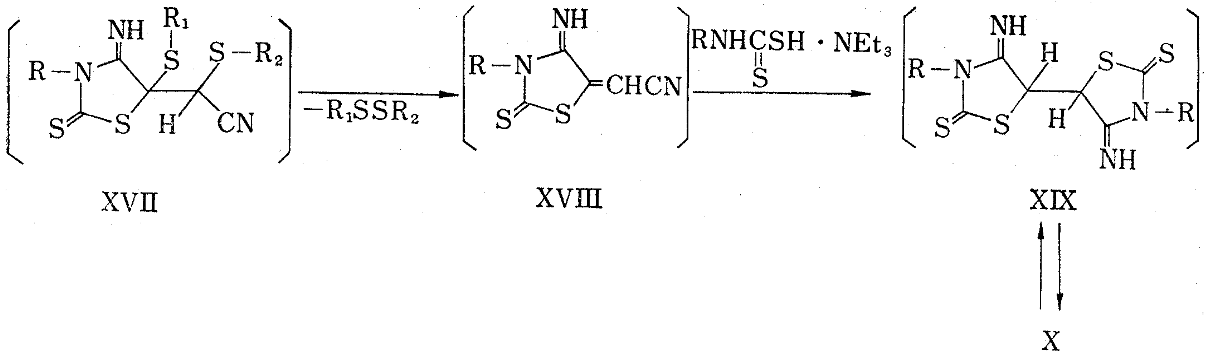


Chart 3

pounds (XVII). XVII would then give XVIII on elimination of disulfides as was observed in the thermal elimination of diethyldisulfide from 2,3-diamino-2,3-bis(ethylthio)succinonitrile.[10] In the reaction of N-methyldithiocarbamate with IXb was isolated dibenzyldisulfide. XVIII is expected to be highly reactive to dithiocarbamates as was observed in the reaction of 5-cyanomethylidene-2-thioxo-4-thiazolidone (XIV) with N-benzyldithiocarbamate described above. Accordingly XIX would be readily formed in the reaction of XVIII with dithiocarbamates. XIX would then tautomerize to X.

Experimental

All melting points are uncorrected. IR spectra were recorded on a Hitachi EPI-S2 spectrometer. UV spectra were determined on a Hitachi EPF-2 spectrometer. NMR spectra were measured with a Varian A-60 spectrometer using tetramethylsilane as internal reference.

General Procedure for the Preparation of 5-Cyanomethyl-2-thioxo-4-aminothiazolines (II). (Method A)——A mixture of fumaronitrile (2.3 g, 29.5 mM) and triethylammonium benzyldithiocarbamate (8.5 g, 30.0 mM) in acetone (50 ml) was heated under reflux for 5 min. After removal of the solvent was added water to the residual brown oily product. The separated solids were collected and washed with water to give 7.4 g of IIc as pale brown solids mp 139—155°. After recrystallization from acetone–water 4.9 g of IIc, mp 164—165° was obtained. Analytical data are given in Table I.

General Procedure for the Preparation of 5-Cyanomethyl-2-thioxo-4-thiazolidones (III). (Method B)——A solution of IIc (2.0 g, 7.7 mM) in conc. HCl (1 ml) and water (20 ml) was heated on a boiling water for 5 min. After cooling on ice the separated crystals were collected and washed with water to give 1.7 g (85.0%) of IIIc as colorless needles, mp 114—116°. After recrystallization from EtOH it melts at 115—116°. Analytical data are given in Table III.

Methanolysis of 3-Benzyl-5-cyanomethyl-4-aminothiazoline (IIc) to 3-Benzyl-5-methoxycarbonylmethyl-2-thioxo-4-thiazolidone (IIIb)——A stirred solution of IIc (0.5 g, 1.91 mM) in MeOH (20 ml) was saturated with dry HCl and heated under reflux for 5 min. After removal of the solvent the residual matter was triturated with water and extracted with benzene. The benzene layer was dried over Na$_2$SO$_4$ and condensed *in vacuo* to give a yellow oil, which solidified on standing after addition of *n*-hexane. The pale yellow crystals of IIIb (0.3 g, 53.1%) which melted at 60—62° were identified with the authentic samples.[3a] In the same manner IIIa was obtained from IIa in a 61% yield and identified with the authentic samples.[3a]

3-Benzyl-5-methoxycarbonimidoylmethyl-2-thioxo-4-thiazolidone (VIII)——A stirred solution of IIIc (3.1 g, 11.8 mM) in MeOH (10 ml) and ether (40 ml) was saturated with dry HCl under cooling on ice. After stirring for 30 min at that temperature the solution was condensed *in vacuo*. The residue was dissolved into ether and diluted with *n*-hexane until the solution became turbid. The separated leaflets were collected and washed with ether to give 3.0 g (77.0%) of VII, mp 105° (decomp). *Anal.* Calcd. for $C_{13}H_{15}O_2N_2S_2Cl$ (VII): C, 47.19; H, 4.57; N, 8.47. Found: C, 46.89; H, 4.46; N, 8.88.

To a stirred solution of VII (1.1 g, 3.3 mM) in MeOH (20 ml) was added 15.5% NH$_3$–MeOH (0.7 ml) at room temperature. After removal of the solvent the residue was triturated with water and extracted with benzene. The benzene layer was dried over Na$_2$SO$_4$ and condensed *in vacuo* to give an oil, which solidified on standing after addition of MeOH. The crystals were collected and washed with small amount of MeOH to give 0.25 g (25.5%) of VIIIa as colorless powder, mp 71—75°. *Anal.* Calcd. for $C_{13}H_{14}O_2N_2S_2$ (VIIIa): C, 53.06; H, 4.80; N, 9.52. Found: C, 53.06; H, 4.80; N, 9.15. Spectral data are given in Table IV.

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[10] O.W. Webster, D.R. Hartter, R.W. Begland, W.A. Sheppard, and A. Cairncross, *J. Org. Chem.*, **37**, 4133 (1972).

3-Benzyl-5-(N-phenylmethoxycarbonimidoylmethyl)-2-thioxo-4-thiazolidone (VIIIb)——A mixture of VII (1.1 g, 13.3 mM) and aniline (0.7 g, 7.52 mM) in MeOH (30 ml) was heated under reflux for 5 min. After removal of the solvent the residue was washed with water and then with *n*-hexane to give 0.8 g (64.5%) of VIIIb, mp 116—119°. *Anal.* Calcd. for $C_{19}H_{18}O_2N_2S_2$ (VIIIb): C, 61.61; H, 4.90; N, 7.56. Found: C, 61.30; H, 4.81; N, 7.74. Spectral data are given in Table IV.

General Procedure for the Preparation of 5,5′-Bi-2-thioxo-4-aminothiazolines (X). (Method C)——To a stirred mixture of 40% aqueous CH_3NH_2 (5.2 g, 67.0 mM) and NEt_3 (6.8 g, 67.4 mM) in EtOH (30 ml) was added dropwise CS_2 (5.4 g, 71.0 mM) over 5 min under cooling (at about 20°). After 30 min IXa (5.1 g, 30.0 mM) was added to the mixture. The solution was heated under reflux for 20 min. After cooling the separated brown solids were collected and washed with acetone and then with water to give 5.5 g (63.0%) of Xa, mp 250° (decomp). After recrystallization from DMF–H_2O it melts at 260° (decomp). Analytical data are given in Table V.

General Procedure for the Autoxidation of 5,5′-Bi-2-thioxo-4-aminothiazolines (X) to $\Delta^{5,5'}$-Bi-2-thioxo-4-iminothiazolidines (XI). (Method D)——A mixture of Xa (0.58 g, 2.0 mM) and NEt_3 (0.1 ml) in DMF (20 ml) was allowed to stand for 3 days. The separated red brown crystals were collected and washed with acetone to give 0.40 g of XIa, mp 270° (decomp). Analytical data are given in Table V.

Reaction of IXb with Triethylammonium N-Methyldithiocarbamate——A mixture of IXb (3.2 g, 9.95 mM) and triethylammonium N-methyldithiocarbamate (4.2 g, 20.2 mM) in EtOH (20 ml) was heated under reflux for 10 min. The separated crystals were collected and washed with acetone to give 1.3 g (44.8%) of Xa, mp 260° decomp. The combined filtrate and washings were left standing for 2 days. The separated crystals were collected and washed with acetone to give 0.3 g (10.3%) of XIa, mp 270° (decomp). The filtrate was condensed *in vacuo* and extracted with hot *n*-hexane (100 ml). The extract was treated with charcoal and condensed *in vacuo* to give 1.6 g of dibenzyldisulfide, mp 55—65°, which melts at 70—71° after recrystallization from ethanol.

Reaction of IXc with Triethylammonium N-Methyldithiocarbamate——A mixture of IXc (1.7 g, 10.1 mM) and triethylammonium N-methyldithiocarbamate (4.2 g. 20.2 mM) in EtOH (20 ml) was heated under reflux for 10 min. The separated crystals were collected and washed with acetone to give 0.6 g (20.7%) of Xa, mp 260° (decomp). The combined filtrate and washings were left standing for 2 days. The separated crystals were collected and washed with acetone to give 0.8 g (27.6%) of XIa, mp 270° (decomp).

Reaction of IXd with Triethylammonium N-Methyldithiocarbamate——A mixture of IXd (1.7 g, 10.1 mM) and triethylammonium N-methyldithiocarbamate (4.2 g, 20.2 mM) in EtOH (20 ml) was heated under reflux for 10 min. The separated crystals were collected and washed with acetone to give 0.75 g (25.9%) of Xa, mp 260° (decomp). The combined filtrate and washings were left standing for 2 days. The separated crystals were collected and washed with acetone to give 0.6 g (20.5%) of XIa, mp 270° (decomp).

Hydrolysis of 3,3′-Dimethyl-5,5′-bi-2-thioxo-4-aminothiazoline (Xa) to 3,3′-Dimethyl-5,5′-2-thioxo-4-thiazolidone (XIIa)——A solution of Xa (0.5 g, 1.73 mM) in 50% H_2SO_4 (20 ml) was heated on a boiling water bath for 30 min. After cooling the separated crystals were collected and washed with water to give 0.45 g (89.4%) of XIIa, mp 218°. XIIa was identical with the authentic sample.[4)] In the same manner Xb was hydrolyzed into XIIb in a 88.0% yield. XIIb was identical with the authentic sample.[3b)]

Hydrolysis of 3,3′-Dibenzyl-5,5′-bi-2-thioxo-4-aminothiazoline (Xc) to 3,3′-Dibenzyl-5,5′-bi-2-thioxo-4-thiazolidone (XIIc)——A suspension of Xc (0.5 g, 1.13 mM) in 50% H_2SO_4 (30 ml) was heated under reflux for 20 hr. After cooling the solids were collected and washed with water. The solids were extracted with acetone to give 0.1 g of Xc. The washings were condensed *in vacuo* to give 0.25 g of XIIc, mp 161°. XIIc was identical with the authentic sample.[3b)]

Hydrolysis of 3,3′-Dimethyl-$\Delta^{5,5'}$-bi-2-thioxo-4-iminothiazolidine (XIa) to 3,3′-Dimethyl-$\Delta^{5,5'}$-bi-2-thioxo-thiazolidone (XIIIa)——A suspension of XIa (0.50 g, 1.74 mM) in 50% H_2SO_4 (30 ml) was heated under reflux for 3 hr. The solids were collected and washed with water to give 0.25 g (50.2%) of XIIIa, mp 316°. XIIIa was identical with the authentic sample.[4)] In the same manner XIIIb was obtained from XIb in a 45.3% yield. XIIIb was identical with the authentic sample.[3b)]

Hydrolysis of 3,3′-Dibenzyl-$\Delta^{5,5'}$-bi-2-thioxo-4-iminothiazolidine (XIc) to 3,3′-Dibenzyl-$\Delta^{5,5'}$-bi-2-thioxo-4-thiazolidone (XIIIc)——A suspension of XIc (0.2 g. 0.454 mM) in 30% HBr–AcOH (10 ml) was heated under reflux for 8 hr. The separated orange-colored crystals were collected and washed with water to give 0.19 g of XIIIc, mp 270°. XIIIc was identical with the authentic sample.[4)]

3-Benzyl-5-cyanomethylidene-2-thioxo-4-thiazolidone (XIV)——A mixture of VIc (1.3 g, 4.96 mM) and Br_2 (0.8 g, 5.00 mM) in AcOH (20 ml) was heated on a boiling water bath for 5 min. After addition of AcONa (0.8 g, 9.75 mM) heating was continued further 10 min. To the mixture was added water and the separated resinous matter was dissolved into hot EtOH (20 ml). After cooling the separated yellow needles were collected and washed with EtOH to give 0.65 g (49.8%) of XIV, mp 82—85°. After recrystallization from *n*-hexane it melts at 83—85°. *Anal.* Calcd. for $C_{12}H_8ON_2S_2$ (XIV): C, 55.39; H, 3.10; N, 10.77. Found: C, 55.22; H, 2.99; N, 10.66. NMR spectrum (δ ppm, $CDCl_3$); 7.35 (C_6H_5-, singlet), 5.26 (CH_2, singlet), 6.38 (C=CH–, singlet). IR spectrum (cm^{-1}, nujol): 2200 (C≡N), 1740 (C=O).

3,3′-Dibenzyl-4-oxo-4′-imino-$\Delta^{5,5'}$-bi-2-thioxo-thiazolidine (XVI)——A mixture of XIV (0.5 g, 1.92 mM) and triethylammonium benzyldithiocarbamate (0.6 g, 2.11 mM) in acetone (20 ml) was stirred at room temp. for 1 hr. The separated green–yellow leaflets were collected and washed with acetone to give 0.35 g (41.3%) of XVI, mp 270° (decomp). *Anal.* Calcd. for $C_{20}H_{15}ON_3S_4$ (XVI): C, 54.43; H, 3.43; N, 9.52. Found: C, 54.74; H, 3.47; N, 9.39. IR spectrum (cm^{-1}, nujol): 3300 (NH), 1700 (C=O), 1630 (C=N).

Hydrolysis of XVI to XIIIc——A suspension of XVI (0.22 g, 0.50 mM) in 30% HBr–AcOH (10 ml) was heated under reflux for 8 hr. The separated red-colored needles were collected and washed with water to give 0.16 g (72.7%) of XIIIc, mp 270°. XIIIc was identical with the authentic sample.[4]

Acknowledgement The author wishes to express his gratitude to Dr. J. Kinugawa for his encouragement throughout this work. Thanks are also due to the members of the Chemical Research Laboratories of the Company for elemental analyses and NMR and UV spectra measurements.