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Heterocyclic Ketenethioacetal Derivatives. VI.[1] Synthesis and Reaction of 2-Bis(methylthio)methylenebenzothiophen-3(2H)-one

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2-Bis(methylthio)methylenebenzothiophen-3(2H)-one, which was prepared by the reaction of benzothiophen-3(2H)-one with carbon disulfide in the presence of sodium hydroxide in dimethyl sulfoxide, reacted with nucleophilic reagents such as amines or active methylenes to give the corresponding the replacement products of one or two methylthio groups in good yields.

In our previous paper, we have reported the synthesis and the reaction of 3-bis(methylthio)methyleneoxindole,[3] 9-methyl-4-bis(methylthio)methylene-1,3-dioxo-1,2,3,4-tetrahydro-β-carboline,[4] 4-bis(methylthio)methylene-1,3-dioxo-1,2,3,4-tetrahydroisoquinolines,[5] and 3-bis(methylthio)methylene-1,4-dioxo-1,2,3,4-tetrahydroisoquinolines.[6] It was found that the methylthio group of these bis(methylthio)methylene derivatives occurred out easily substitution with strong nucleophilic reagents such as amines, active methylenes, and cyano anion to give the corresponding substituted products.[7] We could easily obtained many indole and isoquinoline derivatives by application of these reaction and could find a few interesting reactions. The bis(methylthio)methylene derivatives as electrophiles would be very substantial intermediate compounds.

In the present paper, we report that the synthesis and the reaction of 2-bis(methylthio)-methylenebenzothiophen-3(2H)-one (IV). It is well known that active methylene compounds react with carbon disulfide in the presence some base.[8] In a similar, it was found that carbon disulfide react also with active methylene of heterocyclic compounds.[9]

The reaction of benzothiophen-3(2H)-one (I) with carbon disulfide in the presence of sodium hydride gave two products of mp 300° (II) in 10% yield and mp 121° (III) in 85% yield. This compound (III) was methyl 3-oxo-2,3-dihydrobenzothiophene-2-dithiocarboxylate. This compound was soluble in 10% sodium hydroxide but the compound II was insoluble in 10% sodium hydroxide. Elemental analysis of II was corresponded to $C_{18}H_{18}O_2S_4$= 384.48. The molecular weight of this compound was also supported by mass spectrum (M^+= 384). The infrared (IR) spectrum of this compound showed the absorption at 1650 cm^{-1} due to carbonyl band at β-position of benzothiophene. From these spectral data and elemental analysis, this compound was found to be a desaurin type compound, 2,4-bis(3-oxo-2,3-dihydrobenzothiophen-2-ylidene)-1,3-dithiacetane (II). We have reported in the previous paper

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[1] Part V: K. Mizuyama, Y.Tominaga, Y. Matsuda, and G. Kobayashi, *Yakugaku Zasshi*, **95**, 290 (1975).
[2] Location: *1-14 Bunkyo-machi, Nagasaki 852, Japan.*
[3] G. Kobayashi, S. Furukawa, and Y. Matsuda, *Yakugaku Zasshi*, **86**, 1152 (1966).
[4] G. Kobayashi, Y. Matsuda, R. Natsuki, and Y. Tominaga, *Yakugaku Zasshi*, **92**, 713 (1972).
[5] G. Kobayashi, Y. Matsuda, R. Natsuki, and S. Ueno, *Yakugaku Zasshi*, **93**, 322 (1973).
[6] S. Ueno, Y. Tominaga, R. Natsuki, Y. Matsuda, and G. Kobayashi, *Yakugaku Zasshi*, **94**, 607 (1974).
[7] S. Ueno, Y. Tominaga, Y. Matsuda, and G. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), **22**, 2624 (1974).
[8] K.A. Jensen and L. Henriksen, *Acta Chem. Scand.*, **22**, 1107 (1968).
[9] *a*) H.D. Edwards and J.D. Kendall, *Chem. Abst.*, **45**, 4052*h* (1951); *b*) P. Papini and M. Ridi, *Gazz. Chim. Ital*, **89**, 526 (1959); *c*) P. Papini and G. Auzzi, *Gazz. Chim. Ital*, **96**, 125, 430 (1966); *d*) P. Rioult and J. Vialle, *Bull. Soc. Chim. France*, **1965**, 3315; *e*) R. Philipe and V. Jean, *Bull. Soc. Chim. France*, **1965**, 3312; *f*) G. Matolcsy, P. Sohar, and B. Bordas, *Chem. Ber.*, **104**, 1155 (1971).

syntheses of the desaurin derivative with heterocyclic system, 1,3-dioxoisoquinoline.[5] It is well known that the reaction of the active methylene with the ketone group with carbon disulfide give corresponding desaurin derivatives.[5,10] In the general method, the alkylation of III with dimethyl sulfate in the presence of sodium hydroxide gave a ketenethioacetal derivative, 2-bis(methylthio)methylenebenzothiophen-3(2H)-one (IV) in 50% yield.

The treatment of IV with phosphorus pentasulfide afforded 1,2-dithiolo[4,3-*b*]benzothiophen-3-thione (V) in good yield. This compound V was also obtained from III in a similar manner. This type compound was well known trithione derivatives which react with dipolarophilic reagent to form 1,3-dipole adducts. The compound V reacted with dimethyl acetylenedicarboxylate (DMAD) to give the corresponding 1,3-dipole adduct (VI). This compound VI have the possibility of 1,4-cycloaddition because of diene system having the thioketone group. It has reported the Diels-Alder reaction of the diene containing the thiocarbonyl group with DMAD to afford 1,4-cycloaddition adducts.[11] The reaction of VI with DMAD gave a 1,4-cycloaddition product (VII) of yellow needles of mp 141° in good yield. This compound was also obtained by the reaction of V with excess DMAD in good yield.

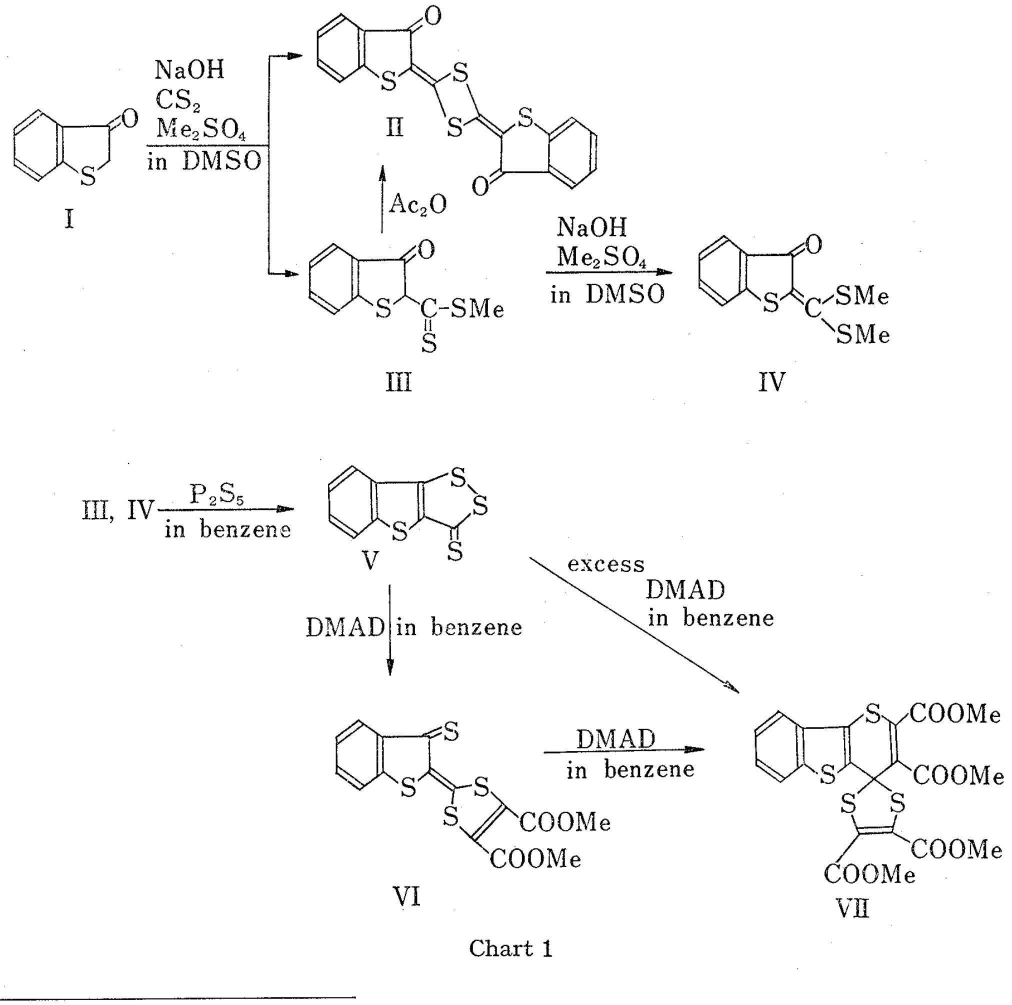

Chart 1

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10) *a*) A Schonberg and L.V. Vargha, *Chem. Ber.*, **64**, 1390 (1931); *b*) A. Schonberg, L.V. Vargha, and H. Kaltschmitt, *Chem. Ber.*, **64**, 2582 (1931); *c*) A. Schonberg, A. Stephenson, H. Kaltschmitt, E. Peterson, and H. Schulten, *Chem. Ber.*, **66**, 237 (1933); *d*) R. Gompper and W. Topfel, *Chem. Ber.*, **95**, 2861 (1962); *e*) A. Schonberg, E. Frese, and K.H. Brosowski, *Chem. Ber.*, **95**, 3077 (1962).

11) *a*) R. Kalish, A.E. Smith, and E.J. Smutny, *Tetrahedron Letters.*, **1971**, 2241; *b*) Y. Tominaga, R. Natsuki, Y. Matsuda, and G. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), **21**, 2770(1973); *c*) Y. Tominaga, K. Mizuyama, and G. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), **22**, 1670 (1970); *d*) G. Kobayashi, Y. Matsuda, Y. Tominaga, and K. Mizuyama, *Heterocycles*, **2**, 309 (1974); *e*) K. Mizuyama, Y. Tominaga, Y. Matsuda, and G. Kobayashi, *Heterocycles*, **2**, 611 (1974).

The reaction of IV with amines (benzylamine, hydrazine hydrate, morpholine, piperidine) afforded amine derivatives, VIII a—d, which were the replaced products of two methylthio groups of compound IV. The IR of VIIIc showed at 1580 cm^{-1} and that of VIIId indicated at 1590 cm^{-1} due to the carbonyl groups on the β-position of thiophene ring for the betain form, VIIIc and d. When the reaction of IV with ammonia afforded (α-amino-α-methylthio)-methylenebenzothiophen-3(2H)-one (IX) which was substituted with only one methylthio group. In the case of the reaction of IV with amines of diamine type (ethylenediamine, *o*-phenylenediamine) gave amine derivatives (Xa, b) which had benzoimidazole ring in good yield. In a similar the reaction of IV with ethanolamine and *o*-aminophenol afforded oxazoline (Xc) and benzoxazole (Xd), respectively. Gompper and the authors[3,12] have reported the substituted reaction of ketenethioacetals with ethylenediamines and ethanolamines to give imidazoline and oxazoline derivatives. Our results were ascribed to belong to the same category with their experiment.

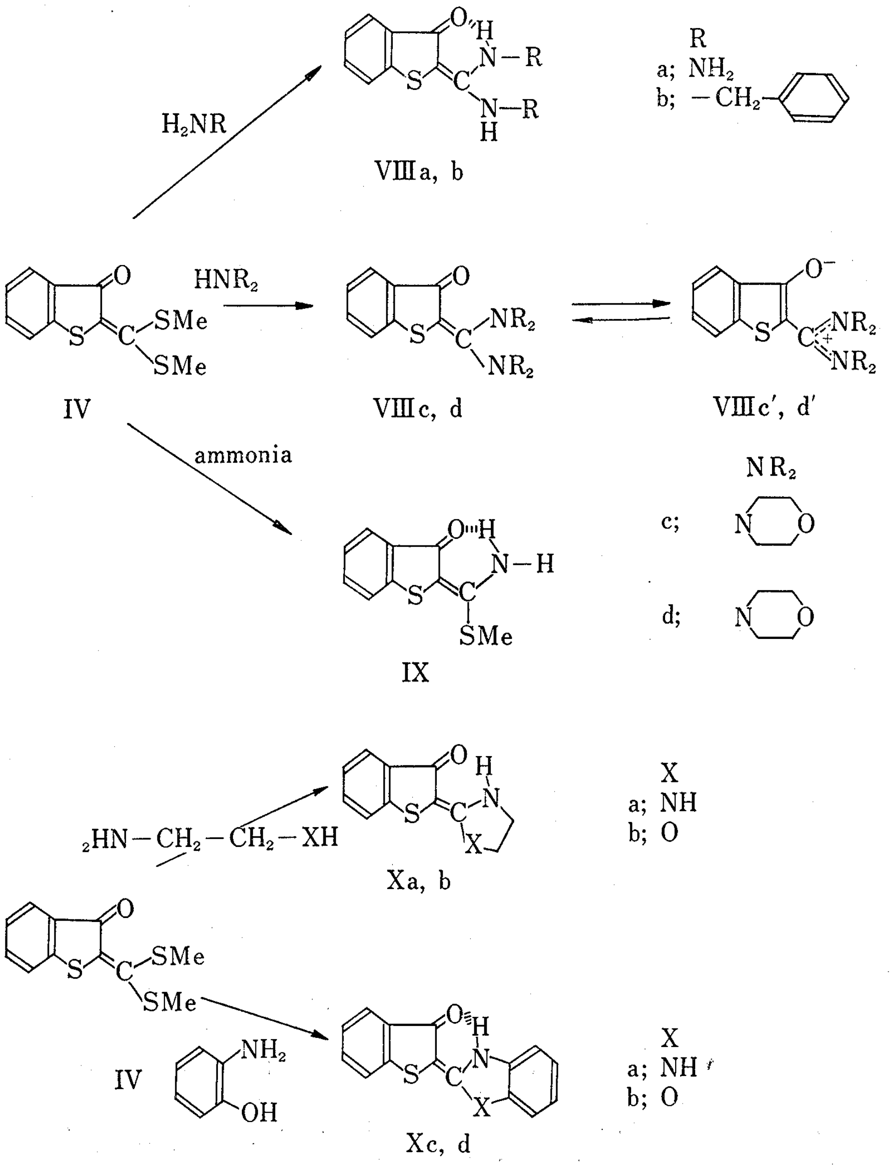

Chart 2

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[12] *a*) R. Gompper and W. Topfel, *Chem. Ber.*, **95**, 2871 (1962); *b*) G. Kobayashi, S. Furukawa, Y. Matsuda, and S. Matsunaga, *Yakugaku Zasshi*, **89**, 203 (1969).

The reaction of IV with methyl cyanoacetate as active methylene in the presence of potassium carbonate in dimethyl sulfoxide gave crystalline powders (XIa), mp 258°, in 80% yield. Elemental analysis of this product corresponded to $C_{13}H_7O_2NS_2$. Its IR spectrum indicated absorption band due to a cyano group at 2200 cm^{-1} and a carbonyl group of pyrone ring at 1615 cm^{-1}. From these spectroscopic data and elemental analysis, this compound of XIa was found to be a cyclized product, 3-cyano-4-methylthiopyrano[3,2-*b*]benzothiophen-2-one. Similary, the compound IV reacted with dimethyl malonate to afford 3-methoxycarbonyl-4-methylthiopyrano[3,2-*b*]benzothiophen-2-one (XIb) of mp 153° in 85% yield. The reaction of IV with acetophenone in the presence of sodium hydroxide instead of potassium carbonate in dimethyl sulfoxide afforded a crystalline powder of mp 173° in 30% yield. Elemental analysis of this product supported a molecular formula of $C_{17}H_{10}O_2S$. Its IR spectrum exhibited an absorption of the carbonyl group at 1650 cm^{-1} and the NMR spectrum of this compound showed on signal due to methyl protons of methylthio group. From these spectral data and elemental analysis, this compound was found to be a cyclized hydrolysis product of methylthio group, 2-phenylpyrano[3,2-*b*]benzothiophen-4-one (XIIa). The reaction of IV with acetylacetone gave also 2-acetyl-3-methylpyrano[3,2-*b*]benzothiophen-4-one (XIIb) of mp 159° in 35% yield. The reaction of IV with nitromethane gave 2-(1-methylthio-2-nitroethylidene)benzothiophen-3(2H)-one (XIII) in good yield.

These substituted products of methylthio group with active methylenes were also obtained by the application of the reaction between I and ketenethioacetal [methyl 2-cyano-3,3-bis(methylthio)acrylate, methyl 2-methoxycarbonyl-3,3-bis(methylthio)acylate, 1-nitro-2,2-

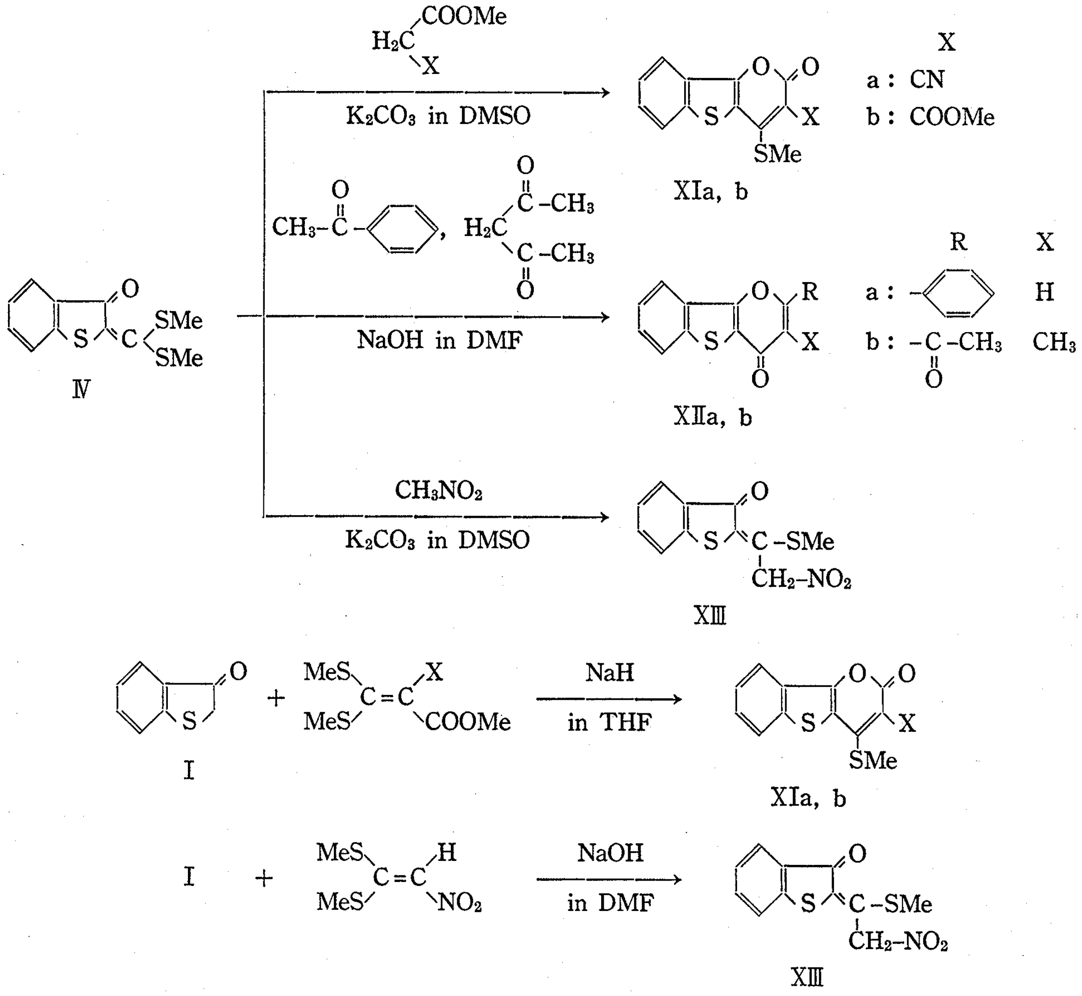


Chart 3

bis(methylthio)ethylene], but these reactions were worse than that of IV with active methylenes.

Since XIa, b, and XIII have active methylthio group for nucleophilic reagents, these compounds are useful synthetic intermediate of benzothiophene derivatives. For example, the reaction of XIa and XIb with amines (benzylamine, cyclohexylamine, ethylenediamine) afforded the amine derivatives, XIVa, b, c, which were the replaced products of methylthio group of compound XIa and XIb in good yield.

The reaction of XIII with ethylenediamine afforded yellow crystal of mp 290° in good yield. The IR and UV spectra agreed with these of VIIIa obtained by the reaction of IV with ethylenediamine.

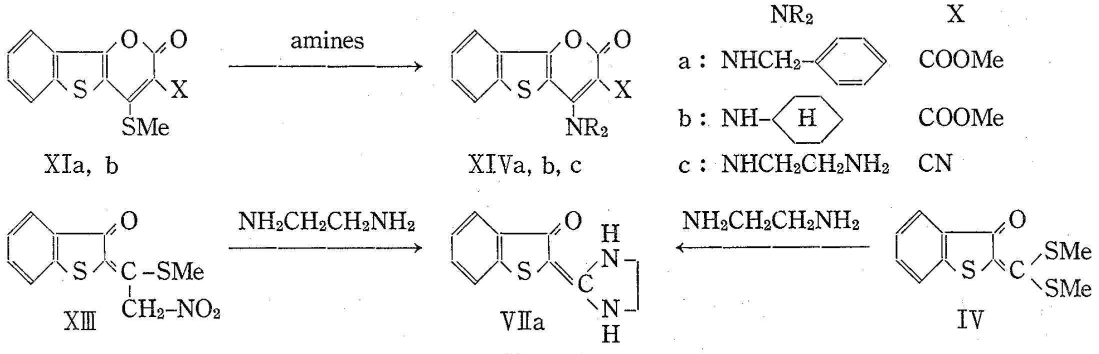


Chart 4

Experimental

All melting points were determined in a capillary and are uncorrected. The IR spectra were recorded in KBr pellets on a Nippon-bunko IRA-2 spectrometer. The UV absorption spectra were determined on a Hitachi EPS-2 spectrometer in 95% EtOH. The NMR spectra were obtained using a JNM-ps-100 (100 Mcps) spectrometer with tetramethylsilane as an internal standard unless otherwise indicated. Mass spectra were recorded on a JEOL JMS-01SG duoble focus mass spectrometer using all cases a direct sample insertion into the ion source.

The Reaction of Benzothiophen-3(2H)-one (I) with CS_2——To a solution of 14 g of I in 100 ml of Me_2SO, conc. NaOH aquation (10 g NaOH in 30 ml of H_2O) was added under stirring and 7.6 g of CS_2 was then added slowly dropwise under stirring over a period of 30 min while the temperature of the mixture was maintained at 5—10°. The reaction mixture was stirred for 1 hr, 1.7 g of Me_2SO_4 was added dropwise with cooling over a period of 20 min, and the reaction mixture was stirred for 1 hr. The mixture was poured into ice-water and the precipitate was collected by filtration, washed with H_2O, and recrystallized from benzene to give a yellow crystal of mp 300° in 8% yield. This compound was a desaurin derivative (II). This filtrate was acidified with 10% HCl. The yellow precipitate was collected, washed with H_2O, and recrystallized from MeOH+benzene to afford methyl 3-oxo-2,3-dihydrobenzothiophen-2-dithiocarboxylate (III) of mp 120—121° in 85% yield. II: yellow needles. *Anal.* Calcd. for $C_{18}H_8O_2S_4$: C, 56.22; H, 2.10; S, 33.36. Found: C, 55.96; H, 2.29; S, 33.41. III: yellow needles. *Anal.* Calcd. for $C_{10}H_8OS_3$: C, 50.01; H, 3.36; S, 39.96. Found: C, 49.92; H, 3.23; S, 39.86. IR(KBr): 1644 cm^{-1} (C=O). UV λ_{max}^{EtOH} nm (log ε): 265 (4.03), 3.46 (4.11), 465 (4.00).

Treatment of III with Ac_2O——A solution of 0.5 g of III in 20 ml of Ac_2O was refluxed for 4—5 hr. The precipitate was appeared, collected by filtration, and recrystallized from pyridine to give yellow crystals of II in 65% yield.

2-Bis(methylthio)methylenebenzothiophen-3(2H)-one (IV)——a) To a solution of 14 g of I in 100 ml of Me_2SO, conc. NaOH aquation (10 g of NaOH in 30 ml of H_2O) was added under stirring and 7.6 g of CS_2 was then added slowly dropwise under stirring over a period of 30 min while the temperature of the mixture was maintained at 5—10°. The reaction mixture was stirred for 1 hr and 35 g of Me_2SO_4 was added dropwise with cooling over a period of 20 min. The mixture was stirred for 2 hr and poured into ice-water. The precipitate was collected by filtration, washed with 5% NaOH and with H_2O, and recrystallized from MeOH to give IV of mp 89—90° in 65% yield.

b) To a solution of 24.1 g of III in 100 ml of Me_2SO, a solution 8 g of NaOH in 20 ml and then 20 g of Me_2SO_4 was added slowly dropwise under stirring at the room temperature. The mixture was stirred for 1 hr at the same temperature and poured into ice-water. The precipitate was collected by filtration, washed with water, and recrystallized from MeOH to give IV in 87% yield. *Anal.* Calcd. for $C_{11}H_{10}OS_3$:

C, 51.97; H, 3.97; S, 37.77. Found: C, 52.03; H, 3.93; S, 37.47. IR(KBr): 1644 cm^{-1} (C=O). UV λ_{max}^{EtOH} nm (log ε): 260 (4.11), 346 (4.14), 465 (4.04). NMR (δ in $CDCl_3$) ppm 2.57 (3H, singlet, SCH_3), 2.62 (3H, singlet, SCH_3).

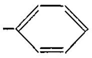
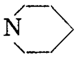
1,2-Dithiolo[4,3-*b*]benzothiophen-3-thione (V)——A mixture of 0.5 g of III or IV, 0.5 g of P_2S_5, and 30 ml of xylene was refluxed for 2 hr. The solution was then filtered while hot. After removal of xylene, the residue was washed with MeOH and recrystallized from benzene to give orange crystals of mp 210° in 30—40% yield. *Anal.* Calcd. for $C_9H_4S_4$: C, 45.01; H, 1.68; S, 53.31. Found: C, 45.10; H, 1.69; S, 53.07. UV λ_{max}^{EtOH} nm (log ε): 320, 450 (slightly soluble in EtOH).

1,3-Dipole Addition Reaction of V with Dimethyl Acetylenedicarboxylate——To a solution of 2.4 g of V in 50 ml of benzene, 1.5 g of dimethyl acetylenedicarboxylate was added. The mixture was heated to reflux for 3 hr. The color of the reaction mixture changed dark violet. Removal of the solvent gave the dark violet needles which were recrystallized from MeOH to give VI of mp 210—212°. *Anal.* Calcd. for $C_{15}H_{10}O_4S_4$: C, 47.08; H, 2.68; S, 33.51. Found: C, 47.01; H, 2.56; S, 32.94. IR (KBr): 1710, 1700 cm^{-1} (C=O). UV λ_{max}^{EtOH} nm: 288 (slightly soluble in EtOH). NMR (δ in $CDCl_3$) ppm: 4.03 (6H, singlet, $2OCH_3$).

1,4-Cycloaddition Reaction of VI with Dimethyl Acetylenedicarboxylate——To a solution of 1.91 g of VI in 50 ml of benzene, 1.4 g of dimethyl acetylenedicarboxylate was added. The mixture was refluxed for 3 hr. The color of the reaction mixture changed from dark violet to yellow. Removal of the solvent gave the yellow needles which were recrystallized from MeOH to give VII of mp 139—141° in 93% yield. *Anal.* Calcd. for $C_{21}H_{16}O_8S_4$: C, 48.10; H, 3.02; S, 24.60. Found: C, 48.02; H, 3.05; S, 24.11. IR (KBr): 1740, 1720, 1710 cm^{-1} (C=O). UV λ_{max}^{EtOH} nm (log ε): 248 (4.20). NMR (δ in $CDCl_3$) ppm: 3.06 (6H, singlet, $2OCH_3$), 3.95 (3H, singlet, OCH_3), 4.00 (3H, singlet, OCH_3).

Reaction of IV with Amines——A mixture of 0.01 mole of IV and 0.025 mole of amines (morpholine, piperidine, benzylamine, hydrazine hydrate) was heated at 150° for 30 min. After cooling, the solid was recrystallized from MeOH or EtOH to give diamine derivatives (the results are shown in Table I).

TABLE I

No.	R	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd. (Found) C	H	N	UV λ_{max}^{EtOH} nm (log ε)	IR (KBr) cm^{-1}
VIIIa	NH_2	87	233	$C_9H_{10}ON_4S$	48.65 (49.23)	4.54 (4.57)	25.22 (25.47)	245 (a)) 282 ( ) 376 ( )	ν_{NH} 3230 3060
VIIIb	CH_2- 	93	196	$C_{23}H_{20}ON_2S$	74.17 (74.11)	5.41 (5.51)	7.52 (8.07)	250 (3.95) 285 (4.16) 385 (3.96)	ν_{NH} 3000
VIIIc		75	188	$C_{17}H_{20}O_3N_2S$	61.43 (60.88)	6.07 (6.18)	8.43 (8.43)	280 (4.15) 318 (4.09) 425 (4.10)	$\nu_{C=O}$ 1580
VIIId		73	176	$C_{19}H_{24}ON_2S$	69.49 (69.80)	7.37 (7.40)	8.53 (9.16)	281 (4.12) 310 (4.06) 418 (4.09)	$\nu_{C=O}$ 1590

a) Concentration is unknown because of insufficient solubility.

Reaction of IV with Ammonia——To a solution of 1 g of IV in 50 ml of MeOH, 10 ml of 28% ammonia water was added and the mixture was refluxed for 30 min. The solvent was evaporated and the residue was recrystallized from MeOH to give yellow needles mp 215° in 55% yield. *Anal.* Calcd. for $C_{10}H_9ONS_2$: C, 53.78; H, 4.06; N, 6.27; S, 28.72. Found: C, 53.83; H, 4.12; N, 6.15,; S, 28.65. UV λ_{max}^{EtOH} nm (log ε): 263 (4.10), 290 (4.10), 321 (4.19), 425 (4.25).

Reaction of IV with Ethylenediamine or Ethanoleamine——To a solution of 2.54 g of IV in 100 ml of MeOH, 0.02 mole of ethylenediamine or ethanolamine was added and the mixture was refluxed for 1 hr. The solvent was evaporated and the residue was washed with ether and recrystallized from MeOH to give oxazoline or imidazoline derivatives (IXa, b) in 80—90% yield. IXa: mp 290°. yellow leaflets. *Anal.* Calcd. for $C_{11}H_{10}ON_2S$: C, 60.54; H, 4.62; N, 12.84. Found: C, 60.50; H, 4.63; N, 12.43. UV λ_{max}^{EtOH} nm (log ε): 248 (3.96), 282 (4.35), 376 (4.11). IXb: mp 167°. yellow needles. *Anal.* Calcd. for $C_{11}H_9O_2NS$: C, 60.27; H, 4.14; N, 6.39. Found: C, 59.92; H, 4.28; N, 6.91. IR (KBr): 3200 cm^{-1} (NH), 1640 cm^{-1} (C–O). UV λ_{max}^{EtOH} nm (log ε): 283 (4.28), 398 (4.04).

Reaction of IV with *o*-Phenylenediamine or *o*-Aminophenol——A mixture of 0.01 mole of IV and 0.01 mole of amines (*o*-phenylenediamine, *o*-aminophenol) was heated at 150° for 1 hr. After cooling, the solid was recrystallized from methylcellosolve to give benzimidazole (Xa) or benzoxazole (Xb) derivatives in 60—

75% yield. Xa: mp 287°. yellow needles. *Anal.* Calcd. for $C_{15}H_{10}ON_2S$: C, 67.66; H, 3.79; N, 10.52; S, 12.02. Found: C, 67.72; H, 3.78; N, 10.48; S, 11.82. IR (KBr): 3600—2400 cm^{-1} (broad). UV λ_{max}^{EtOH} nm (log ε): 255 (4.12), 325 (4.36), 343 (4.35), 360 (4.32), 400 (4.12). Xb: mp 250°. brown needles. *Anal.* Calcd. for $C_{15}H_9O_2NS$: C, 67.41; H, 3.39; N, 5.24. Found: C, 67.28; H, 3.36; N, 5.26. UV λ_{max}^{EtOH} nm (log ε): 240 (4.16), 268 (4.51), 325 (4.51), 347 (4.50).

4-Methylthiopyrano[3,2-*b*]benzothiophen-2-ones (XIa, b)——a) To a solution of 0.02 mole of active methylene (methyl cyanoacetate, dimethyl malonate) and 0.03 mole of K_2CO_3 in 30 ml of Me_2SO, 0.01 mole of IV was added with stirring at room temperature for 3 hr. The color of the reaction mixture turned reddish brown. The mixture was poured into ice-water and acidified with 10% HCl solution. The precipitate was collected by filtration, washed with water, and recrystallized from MeOH or acetone to give pyrano-[3,2-*c*]benzothiophen-2-ones (XIa, b) in a high yield such as 70—80% yield.

b) To a suspension of 0.96 g (0.01 mole) of NaH in mineral oil in 50 ml of absolute THF, 0.01 mole of I and ketenethioacetal (methyl 2-cyano-3,3-bis(methylthio)acrylate, methyl 2-methoxycarbonyl-3,3-bis-(methylthio)acrylate) were added. The mixture was refluxed on the boiling water bath for 2 hr. After the solvent was evaporated, 200 ml of ice-water was added to its residue and acidified with 10% HCl solution. The precipitate was collected by filtration, washed with water, and recrystallized from MeOH, or acetone to give IXa or b in 40—60% yield. IXa: mp 258°. yellow needles. *Anal.* Calcd. for $C_{13}H_7ONS_2$: C, 57.15; H, 2.58; N, 5.13; S, 23.47. Found: C, 57.27; H, 2.69; N, 4.92; S, 23.44. IR (KBr): 1615 cm^{-1} (C=O). UV λ_{max}^{EtOH} nm: 267, 336, 390, (concentration is unknown because of insufficient solubility). XIb: mp 153°. Yellow leaflets. *Anal.* Calcd. for $C_{14}H_{10}O_4S_2$: C, 57.15; H, 2.58; N, 5.13; S, 23.47. Found: C, 57.27; H, 2.69; N, 4.92; S, 23.44. IR (KBr): 1730 cm^{-1} (C=O of ester group), 1685 cm^{-1} (C=O of pyrone ring). UV λ_{max}^{EtOH} nm (log ε): 266 (4.19), 330 (4.16).

2-Phenylpyrano[3,2-*b*]benzothiophen-4-one (XIIa)——To a solution of 0.5 g of IV in 30 ml of dimethyl formamide, 0.5 g of acetophenone and 0.04 g of powder NaOH were added with stirring at room temperature. The mixture was stirred at room temperature for 3 hr, poured into ice-water, and acidified with 10% HCl solution. The precipitate was collected by filtration, washed with water, and recrystallized from MeOH to give a brown needles of mp 173° in 35% yield. *Anal.* Calcd. for $C_{17}H_{10}O_2S$: C, 73.30; H, 3.62; S, 11.50. Found: C, 72.81; H, 3.65; S, 11.42. IR (KBr): 1650 cm^{-1} (C=O). UV λ_{max}^{EtOH} nm (log ε): 236 (4.30), 273 (4.39), 302 (4.37).

2-Acetyl-3-methylpyrano[3,2-*b*]benzothiophen-4-one (XIIb)——To a solution of 0.3 g of IV in 30 ml of dimethyl formamide, 0.08 g of powder NaOH and 0.2 g of acetylacetone were added. The mixture was heated on the boiling water bath for 2 hr. After cooling, the mixture was poured into 150 ml of ice-water and acidified with 10% HCl solution. The precipitate was collected by filtration, washed with water, and recrystallized from MeOH to give brown needles of mp 159° in 25% yield. *Anal.* Calcd. for $C_{14}H_{10}O_3S$: C, 65.12; H, 3.90; S, 12.39. Found: C, 64.42; H, 3.86; S, 12.42. IR (KBr): 1630 cm^{-1}(C=O).

2-(1-Methylthio-2-nitroethylidene)benzothiophen-3(2H)-one (XIII)——a) To a solution of 2.5 g of IV and 0.8 g of nitromethane in 50 ml Me_2SO, 1.65 g of K_2CO_3 was added with stirring at room temperature. The mixture was stirred at room temperature for 3 hr when the mixture turned reddish brown. The mixture was poured into ice-water and acidified with 10% HCl solution. The precipitate was collected by filtration and recrystallized from MeOH to give a yellow needles of mp 142° in 85% yield.

b) To a solution of 1.5 g of I in 50 ml of Me_2SO, 1 g of powder NaOH and 1.6 g of 1-nitro-2,2-bis(methylthio)ethylene were added. The mixture was stirred at room temperature, poured into ice-water, and acidified with 10% HCl solution. The resulting precipitate was collected by filtration and recrystallized from MeOH to give yellow needles of mp 142° in 63% yield. *Anal.* Calcd. for $C_{11}H_9O_3NS_2$: C, 49.44; H, 3.40; N, 5.24. Found: C, 50.00; H, 3.40; N, 5.06. IR (KBr): 1650 cm^{-1} (C=O). UV λ_{max}^{EtOH} nm (log ε): 258 (4.18), 342 (4.16), 443 (3.94). NMR (δ in $CDCl_3$) ppm: 6.08 (2H, singlet, CH_2–NO_2), 2.64 (3H, singlet, SCH_3).

Reaction of XIa, b with Amines——To a solution of 0.01 mole of XIa or XIb in 50 ml of MeOH, 0.015 mole of amines (benzylamine, cyclohexylamine, ethylenediamine) was added. The mixture was refluxed on the boiling water for 1 hr. After the solvent was evaporated, 50 ml of ice-water was added to the residue and the mixture was acidified with 10% HCl solution to remove excess amines. Resulting precipitate was collected and recrystallized from MeOH or methylcellosolve to give amine derivatives in 70—80% yield. XIVa: colorless needles. mp 272°. *Anal.* Calcd. for $C_{20}H_{15}O_4NS$: C, 65.75; H, 4.14; N, 3.85. Found: C, 65.77; H, 4.08; N, 3.68. IR (KBr): 3040 cm^{-1} (NH). UV λ_{max}^{EtOH} nm 234, 308, 338 (concentration is unknown because of insufficient solubility). XIVb: colorless needles. mp 218°. *Anal.* Calcd. for $C_{19}H_{19}O_4NS$: C, 63.86; H, 5.36; N, 3.92. Found: C, 63.31; H, 5.12; N, 3.64. IR (KBr): 3040 cm^{-1} (NH), 1720 cm^{-1} (C=O). UV λ_{max}^{EtOH} nm (log ε): 233 (4.62), 304 (4.34), 333 (4.39). XIVc: yellow needles. mp 204°. *Anal.* Calcd. for $C_{14}H_{11}O_2N_3S$: C, 58.94; H, 3.89; N, 14.73. Found: C, 58.52; H, 4.02; N, 14.43. IR (KBr): 3280, 3340 cm^{-1} (NH), 2200 cm^{-1} (CN), 1770 cm^{-1} (C=O). UV λ_{max}^{EtOH} nm (log ε): 230 (4.54), 260 (4.29), 300 (4.31), 326 (4.30).

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