Reactions of 4-Chloro-5*H*-1,2,3-dithiazole-5-thione with α,β-Unsaturated β-Amino Esters: Formation of 2-[2-(1-Alkenylsulfanyl-1-alkoxycarbonyl-2-amino)-1,2-dicyano-vinylsulfanyl]- 3-amino-2-alkenoic Alkyl Esters

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Treatment of 4-chloro-5*H*-1,2,3-dithiazole-5-thione with alkyl 3-alkyl (or aryl)-3-amino-2-propenoates in the presence of pyridine (2 equivalents) in dichloromethane at reflux gave 2-[2-(1-alkenylsulfanyl-1-alkoxy-carbonyl-2-amino)-1,2-dicyanovinylsulfanyl]- **4** and –1,2-dicyanovinyldisulfanyl]-3-amino-2-alkenoic alkyl esters **7** in 16 to 60% and 8 to 48% yields, respectively.

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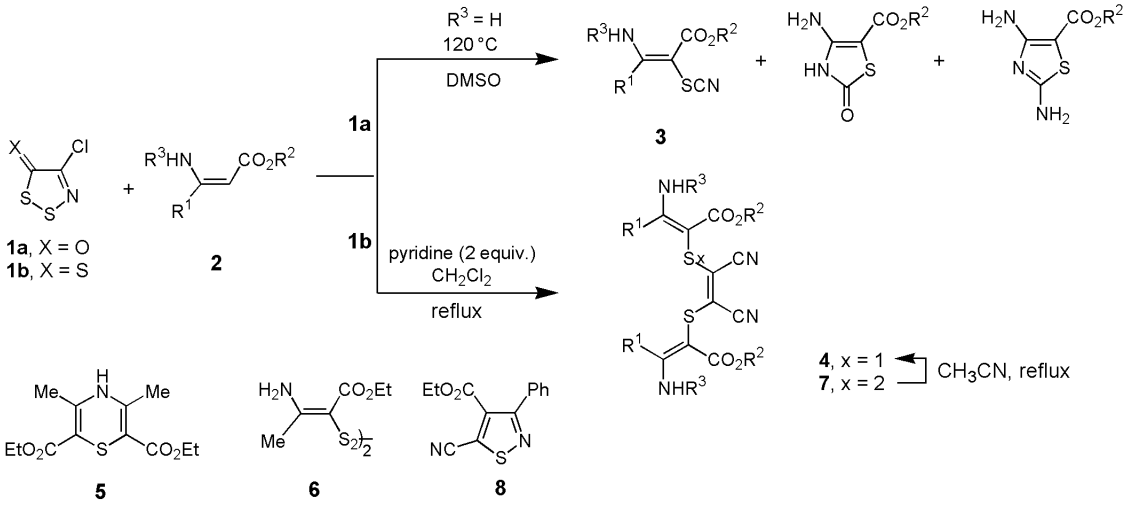
Previously we reported that 4-chloro-5*H*-1,2,3-dithiazol-5-one **1a** acted as a good α-thiocyanating agent for α,β-unsaturated β-amino esters **2** (R^3 = H), yielding alkyl 3-amino-2-thiocyanato-2-alkenoates **3** (R^3 = H) [1] (Scheme 1). This result prompted us to investigate the reactivity of 4-chloro-5*H*-1,2,3-dithiazole-5-thione (**1b**) [2], analogous to **1a**, toward the same β-enamino esters. The results are described herein.

Scheme 1



Results and Discussion.

Treatment of compound **1b** with compound **2b** (R^1 = Me, R^2 = Et, R^3 = H) (2.6 equivalents) in dimethyl sulfoxide (10 ml) for 4 days at room temperature gave 3-amino-2-[2-(2-amino-1-ethoxycarbonylpropenylsulfanyl)-1,2-dicyanovinylsulfanyl]-2-butenoic ethyl ester **4b** (x = 1, R^1 = Me, R^2 = Et, R^3 = H) (18%) together with 1,4-thiazine derivative **5** (10%), tetrasulfide **6** (13%), a minute amount of sulfur, and unknown mixtures, which were inseparable by chromatography and high performance liquid chromatography [(μBodapak C18, 10 μm, 7.8 x 300 mm ID), differential refractometer, acetonitrile]. Of the isolated compounds, compound **5** was obtained by treatment of compound **1a** with compound **2b** under the same conditions [1].

A survey of the literature shows that *cis*-bis(2,3-dialkylthio)-2-butenedinitriles such as 1,2-dicyano-3,6-dithiacyclohexene [3] and *cis*-2,3-bis(benzylthio)-2-butenedinitrile [4], analogous to compound **4b** as far as the bis(2,3-dithio)-2-butenedinitrile moiety is concerned, are important as starting materials for the synthesis of alkylthioporphyrazines.

The reaction was completed in 24 hours at 40 °C under the same conditions to give somewhat increased yields of compounds **4b** (27%) and **5** (40%) along with sulfur, unknown mixtures, and unreacted β-amino esters **2b** (11%). No compound **6** was detected. The reaction did not proceed in dichloromethane at reflux temperature. Heating compounds **1b**, **2b**, and pyridine (2 equivalents) in dichloromethane for

24 hours at reflux resulted in the formation of **4b** (33%), **5** (11%), sulfur, and an unknown mixture with recovery of unreacted **2b** (5%). Notably, an additional new compound **7b** (x = 2, R^1 = Me, R^2 = Et, R^3 = H), having three sulfur atoms, was isolated in 8% yield (Scheme 1).

Compound **4b** was a powder-type of solid, which showed eight ^{13}C nmr (75 MHz, deuteriochloroform) signals and had mass number (*m*/*z*) 396, corresponding to the molecular weight of a compound having the molecular formula $C_{16}H_{20}N_4O_4S_2$. The spectroscopic data indicates that compound **4b** is a symmetric molecule. All other data including ^1H nmr and elemental analysis are compatible with the expected structure. For compound **7b**, fab ms had mass number (*m*/*z*) 429 ($M^+ + 1$). The mass number of the molecular ion (M^+) is 32 units greater than the molecular weight of compound **4b**, and sixteen ^{13}C nmr signals, twice the number of those exhibited by compound **4b**, were observed. The ^1H nmr (300 MHz, deuteriochloro-

Table 1

Reaction Conditions and Yields and Melting Points of Compounds **4** and **7**

	Compounds **2**			Compound **1b**		Temp	Time	Compounds **4**			Compounds **7**			S_8
	R^1	R^2	R^3	mmoles	mmoles	[a]	hours		Yield (%)	Mp (°)		Yield (%)	Mp (°)	mg
a	Me	Me	H	1.24	0.78	rt	15	**a**	16	184-186(dec) [b]	**a**	48	140-142 [b]	8
b	Me	Et	H	1.56	0.97	reflux	24	**b**	33 [d]	173-176 [b]	**b**	8	liquid	25
c	Et	Et	H	0.85	0.71	reflux	7	**c**	28	168-169 [c]	**c**	22	liquid	22
d	CF_3	Et	H	2.45	1.66	reflux	192	**d**	0		**d**	34	liquid	58
e	Ph	Et	H	0.81	0.60	reflux	13	**e**	28 [e]	168-170 [b]	**e**	29	liquid	24
f	4-$MeOC_6H_4$	Et	H	1.86	0.83	reflux	20	**f**	60	162-164 [b]	**f**	0		38
g	4-MeC_6H_4	Et	H	0.99	0.85	reflux	19	**g**	23	206-208 [b]	**g**	29	liquid	21
h	4-BrC_6H_4	Et	H	0.73	0.61	reflux	14	**h**	27	liquid	**h**	27	liquid	22
i	3-$NO_2C_6H_4$	Et	H	0.69	0.60	reflux	19	**i**	29	218-220 [b]	**i**	31	liquid	15
j	Me	Et	Bn	1.00	0.85	rt	14	**j**	13	136-138 [c]	**j**	0		23
k	Me	Et	*i*-Pr	2.84	1.40	rt	9	**k**	30	liquid	**k**	0		22
l	Me	Et	4-ClC_6H_4	1.49	1.24	rt	7	**l**	11	182-184 [c]	**l**	0		50

[a] Apart from the reactions with compounds **2b-i**, the reactions with compounds **2a** and **2j-l** occurred at room temperature (rt). [b] From a mixture of dichloromethane and *n*-hexane. [c] From a mixture of chloroform and *n*-hexane. [d] In addition, 2,6-diethoxycarbonyl-3,5-dimethyl-1,4-thiazine **5** (11%) was isolated. [e] In addition, 4-ethoxycarbonyl-3-phenylisothiazole-5-carbonitrile **8** (36%) was isolated.

Table 2

^1H and ^{13}C NMR, IR, and MS Spectral and Analytical Data of **4** and **7**

Compounds	^1H NMR (deuteriochloroform) δ (ppm)	^{13}C NMR (deuteriochloroform) δ (ppm)	IR (neat) (cm^{-1})	FAB MS (m/z, %)	Molecular Formula	Analyses % Calcd/Found C	H	N	S
4a [b]	2.22 (s, 6H, $2CH_3$), 3.61 (s, 6H, $2OCH_3$), 8.57 (s, 2H, 2NH), 9.17 (s, 2H, 2NH)	22.7, 52.1, 77.4, 113.4, 124.5, 169.4, 171.4	3440, 3312, 3232, 2208, 1648	369 ($M^+ + 1$)	$C_{14}H_{16}N_4O_4S_2$	45.56 45.64	4.38 4.48	15.21 15.34	17.41 17.22
4b [b]	1.30 (t, 6H, J = 7.1 Hz, $2CH_3$), 2.46 (s, 6H, $2CH_3$), 4.21 (q, 4H, J = 7.1 Hz, $2OCH_2$), 5.43 (s, 2H, 2NH), 9.27 (s, 2H, 2NH)	14.7, 23.6, 61.0, 80.9, 112.9,124.3, 169.3, 169.4	3440, 3328, 2208, 1645, 1619, 1606, 1514, 1216, 1165, 1059, 774	397 ($M^+ + 1$)	$C_{16}H_{20}N_4O_4S_2$	48.42 48.47	5.08 5.10	14.13 14.23	16.18 16.01
4c [b]	1.25 (t, 6H, J = 7.6 Hz, $2CH_3$), 1.32 (t, 6H, J = 7.1 Hz, $2CH_3$), 2.67 (q, 4H, J = 7.6 Hz, 2 x CH_2), 4.22 (q, 4H, J = 7.1 Hz, 2 OCH_2), 5.74 (s, br, 2H, 2 NH), 9.52 (s, 2H, br, 2 NH)	12.2, 14.4, 29.3, 60.6, 79.4,112.6, 124.0, 169.1, 173.5	3456, 3328, 3232, 2208, 1648, 1619	425 ($M^+ + 1$)	$C_{18}H_{24}N_4O_4S_3$	50.92 50.85	5.70 5.72	13.20 13.40	15.11 15.25
4e [b]	1.26 (t, 6H, J = 7.1 Hz, $2CH_3$), 4.19 (q, 4H, J = 7.1 Hz, $2OCH_2$), 5.53 (br, s, 1H,NH), 5.55 (s, br, 1H, NH), 7.30–7.45 (m, 10H, ArH), 9.42 (s, br, 2H, 2NH)	14.4, 60.8, 81.5, 112.8, 123.6, 127.6, 128.5, 129.9, 137.0, 169.0, 169.9	3408, 3296, 2208, 1651, 1590	520 (M^+)	$C_{26}H_{24}N_4O_4S_2$	59.98 60.11	4.65 4.64	10.76 10.92	12.32 12.20
4f [b]	1.25 (t, 6H, J = 7.1 Hz, $2CH_3$), 3.82 (s, 6H, $2OCH_3$), 4.17 (q, 4H, J = 7.1 Hz, $2OCH_2$), 5.70 (s, br, 2H, 2NH), 6.89 (d, 4H, J = 8.7 Hz, ArH), 7.27 (d, 4H, J = 8.7 Hz, ArH), 9.40 (s, br, 2H, 2NH)	14.7, 55.8, 61.1, 81.4, 113.3, 114.2, 124.0, 129.5, 129.8, 161.1, 169.5, 170.2	3408, 3296, 2976, 2208, 1651, 1597	580 (M^+)	$C_{28}H_{28}N_4O_6S_2$	57.92 57.94	4.86 4.90	9.65 9.55	11.04 11.22

Table 2 (continued)

Compounds	^{1}H NMR (deuteriochloroform) δ (ppm)	^{13}C NMR (deuteriochloroform) δ (ppm)	IR (neat) (cm^{-1})	FAB MS (m/z, %)	Molecular Formula	Analyses % Calcd/Found C	H	N	S
4g [b]	1.27 (t, 6H, J = 7.0 Hz, 2CH_3), 2.38 (s, 6H, 2CH_3), 4.19 (q, 4H, J = 7.1 Hz, 2CH_2), 5.51 (s, br, 2H, 2NH), 7.13–7.24 (m, 8H, ArH), 9.42 (s, br, 2H, 2NH)	14.3, 21.4, 60.7, 81.4, 112.9, 123.7, 127.6, 129.2, 134.2, 140.1, 169.0, 170.0	3360, 3280, 2976, 2208, 1648	548 (M^+)	$C_{28}H_{28}N_4O_4S_2$	61.29 61.35	5.14 5.16	10.21 10.32	11.69 11.54
4h	1.27 (t, 6H, J = 7.1 Hz, 2CH_3), 4.21 (q, 4H, J = 7.1 Hz, 2OCH_2), 5.57 (s, br, 2H, 2NH), 7.24 (d, 4H, J = 8.4 Hz, ArH), 7.58 (d, 4H, J = 8.4 Hz, ArH), 9.42 (s, br, 2H, 2NH)	14.3, 60.9, 81.7, 112.7, 123.5, 124.4, 129.3, 131.9, 135.6, 168.7, 168.7	3424, 3296, 2976, 2208, 1651, 1590	678 (M^+)	$C_{26}H_{22}Br_2N_4O_4S_2$	46.03 46.18	3.27 3.30	8.26 8.22	9.45 9.60
4i [b]	1.26 (t, 6H, J = 7.1 Hz, 2CH_3), 4.22 (q, 4H, J = 7.1 Hz, 2OCH_2), 5.68 (s, br, 2H, 2NH), 7.60–7.73 (m, 4H, ArH), 8.18 (s, 2H, ArH), 8.30 (d, 2H, J = 7.7 Hz, ArH), 9.46 (s, br, 2H, 2NH)	14.2, 61.2, 82.4, 112.5, 122.9, 123.4, 124.8, 130.0, 133.8, 138.0, 147.9, 166.9, 168.4	3408, 3296, 2976, 2208, 1654, 1590	610 (M^+)	$C_{26}H_{22}N_6O_8S_2$	51.14 51.22	3.63 3.63	13.76 13.82	10.50 10.55
4j [b]	1.28 (t, 6H, J = 7.0 Hz, 2CH_3), 2.34 (s, 6H, 2CH_3), 4.18 (q, 4H, J = 7.1 Hz, 2OCH_2), 4.55 (d, 4H, J = 6.0 Hz, 2CH_2), 7.28-7.40 (m, 10H, ArH), 10.71 (s, br, 2H, 2NH)	14.8, 18.1, 48.7, 60.9, 79.9, 113.0, 124.6, 127.2, 128.2, 129.5, 137.2, 170.2, 170.6	3200, 2992, 2224, 1638, 1578	576 (M^+)	$C_{30}H_{32}N_4O_4S_2$	62.48 62.58	5.59 5.60	9.71 9.64	11.12 11.24
4k	1.24–1.31 (m, 18H, 6CH_3), 2.34 (s, 6H, 2CH_3), 3.80–3.84 (m, 2H, 2CH), 4.17 (q, 4H, J = 7.1 Hz, 2OCH_2), 10.34 (s, 2H, 2NH)	14.5, 17.5, 23.6, 46.5, 60.3, 77.9, 112.7, 124.3, 168.6, 170.0	3216, 2976, 2208, 1677	480 (M^+)	$C_{22}H_{32}N_4O_4S_2$	54.98 55.14	6.71 6.75	11.66 11.60	13.34 13.28
4l [b]	1.33 (t, 6H, J = 7.1 Hz, 2CH_3), 2.29 (s, 6H, 2CH_3), 4.24 (q, 4H, J = 7.1 Hz, 2OCH_2), 7.10 (d, 4H, J = 8.6 Hz, ArH), 7.37 (d, 4H, J = 8.6 Hz, ArH), 11.87 (s, 2H, 2 NH)	14.4, 19.3, 60.9, 82.4, 112.5, 123.9, 127.3, 129.6, 132.9, 136.6, 168.2, 169.6	3168, 2976, 2208, 1632, 1581	616 (M^+ +1)	$C_{28}H_{26}Cl_2N_4O_4S_2$	54.46 54.44	4.24 4.24	9.07 9.03	10.38 10.42
7a [a] [b]	2.26 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 3.74 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 5.67 (s, br, 2H, 2 NH), 9.43 (s, br, 2H, 2NH)	23.2, 23.5, 51.6, 51.9, 80.2, 88.6, 112.0, 114.1, 119.4, 133.5, 169.1, 169.2, 169.5, 170.0	3424, 3296, 2208, 1668	401 (M^+ + 1)	$C_{14}H_{16}N_4O_4S_3$	41.99 42.12	4.03 4.13	13.99 13.82	24.02 24.11
7b	1.28 (t, 3H, J = 7.3 Hz, CH_3), 1.37 (t, 3H, J = 7.1 Hz, CH_3), 2.22 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 4.17–4.25 (m, 4H, 2OCH_2), 5.87 (s, br, 1H, NH), 5.92 (s, br, 1H, NH), 9.38 (s, br, 1H, NH), 9.40 (s, br, 1H, NH)	14.8, 14.9, 23.4, 23.8, 60.9, 61.0, 80.5, 88.9, 112.5, 114.7, 119.5, 134.5, 169.2, 169.5, 170.0, 170.1	3408, 3312, 2208, 1651	429 (M^+ + 1)	$C_{16}H_{20}N_4O_4S_3$	44.84 44.72	4.70 4.74	13.07 13.20	22.45 22.35
7c	1.18–1.32 (m, 9H, 3CH_3), 1.39 (t, 3H, J = 7.1 Hz, CH_3), 2.56 (q, 2H, J = 7.6 Hz, CH_2), 2.86 (q, 2H, J = 7.5 Hz, CH_2), 4.16– 4.28 (m, 4H, 2OCH_2), 5.80 (s, br, 2H, 2NH), 9.52 (s, br, 2H, 2NH)	12.2, 12.6, 14.4, 14.5, 29.2, 29.3, 60.6, 60.6, 79.2, 87.7, 112.1, 114.2, 119.4, 133.9, 169.0, 170.0, 173.6, 174.4	3424, 3312, 2976, 2224, 1648, 1600	457 (M^+ + 1)	$C_{18}H_{24}N_4O_4S_3$	47.35 47.42	5.30 5.34	12.27 12.24	21.07 21.20
7d	1.29 (t, 3H, J = 7.3 Hz, CH_3), 1.40 (t, 3H, J = 7.2 Hz, CH_3), 4.24–4.35 (m, 4H, 2OCH_2), 6.37 (s, br, 2H, 2NH), 9.60 (s, br, 2H, 2NH)	13.0, 13.3, 60.9, 61.0, 81.2, 89.7, 110.5, 112.7, 117.8 (q, J = 278.0 Hz), 118.3, 118.6 (q, J = 279.2 Hz), 136.1, 153.8 (q, J = 30.6 Hz), 154.3 (q, J = 30.6 Hz), 167.0, 167.9	3408, 3264, 2992, 2208, 1667, 1603	537 (M^+ + 1)	$C_{16}H_{14}F_3N_4O_4S_3$	35.82 36.01	2.63 2.61	10.44 10.62	17.93 17.85
7e	1.30 (t, 3H, J = 7.1 Hz, CH_3), 1.38 (t, 3H, J = 7.0 Hz, CH_3), 4.23–4.30 (m, 4H, 2OCH_2), 5.54 (s, br, 1H, NH), 5.60 (s, br, 1H, NH), 7.27–7.46 (m, 10H, ArH), 9.40 (s, br, 1H, NH), 9.51 (s, br, 1H, NH)	14.8, 14.9, 61.3, 61.4, 81.8, 90.5, 112.8, 114.1, 119.6,128.0, 128.3, 129.0, 129.1,130.5, 130.6, 133.7, 137.1,137.4, 169.3, 170.3, 170.7, 171.0	3424, 3296, 2208, 1651, 1590, 1504	553 (M^+ + 1)	$C_{26}H_{24}N_4O_4S_3$	56.50 56.48	4.38 4.35	10.14 10.32	17.41 17.55

form) spectrum showed two triplets at 1.28 and 1.37 ppm and two singlets at 2.22 and 2.45 ppm due to the presence of two ethoxycarbonyl groups and two methyl groups bonded to two C=C double bonds, respectively. The spectroscopic data indicates that compound **7b** is an unsymmetric molecule having the molecular formula

Table 2 (continued)

Compounds	^{1}H NMR (deuteriochloroform) δ (ppm)	^{13}C NMR (deuteriochloroform) δ (ppm)	IR (neat) (cm^{-1})	FAB MS (m/z, %)	Molecular Formula	Analyses % Calcd/Found C	H	N	S
7g	1.31 (t, 3H, J = 7.1 Hz, CH_3), 1.37 (t, 3H, J = 7.1 Hz, CH_3), 2.35 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 4.22–4.29 (m, 4H, $2OCH_2$), 5.47 (s, br, 1H, NH), 5.57 (s, br, 1H, NH), 7.19–7.24 (m, 8H, ArH), 9.40 (s, br, 1H, NH), 9.48 (s, br, 1H, NH)	14.3, 14.4, 21.4, 21.4, 60.7, 60.8, 81.4, 90.0, 112.3, 114.0, 119.0, 127.6, 127.9, 129.2, 129.3, 130.4, 133.3, 134.0, 140.3, 140.5, 168.9, 170.0, 170.4, 170.8	3408, 3280, 2928, 2208, 1651, 1590	581 (M^+ + 1)	$C_{28}H_{28}N_4O_4S_3$	57.91 58.03	4.86 4.87	9.65 9.57	16.56 16.49
7h	1.29 (t, 3H, J = 6.9 Hz, CH_3), 1.37 (t, 3H, J = 7.1 Hz, CH_3), 4.21–4.31 (m, 4H, $2OCH_2$), 5.59 (s, br, 1H, NH), 5.63 (s, br, 1H,NH), 7.17 (d, 2H, J = 8.3 Hz, ArH), 7.24 (d, 2H, J = 8.3 Hz, ArH), 7.58 (d, 4H, J = 8.3 Hz, ArH), 9.40 (s, br, 1H, NH), 9.46 (s, br, 1H, NH)	14.3, 14.5, 60.9, 61.1, 81.7, 90.1, 112.2, 113.7, 119.1, 124.1, 126.5, 129.3, 129.5, 131.8, 132.0, 133.2, 135.5, 135.7, 168.7, 168.9, 169.3, 169.6	3392, 3208, 2976, 2208, 1648, 1590	711 (M^+ + 1)	$C_{26}H_{22}Br_2N_4O_4S_3$	43.95 44.13	3.12 3.18	7.89 7.80	13.54 13.42
7i	1.28 (t, 3H, J = 6.8 Hz, CH_3), 1.34 (t, 3H, J = 6.8 Hz, CH_3), 4.18–4.30 (m, 4H, $2OCH_2$), 5.78 (s, br, 1H, NH), 5.91 (s, br, 1H, NH), 7.65–7.75 (m, 4H, ArH), 8.16 (s, 1H, ArH), 8.23 (s, 1H, ArH), 8.31–8.33 (m, 2H, ArH), 9.39 (s, br, 1H, NH), 9.50 (s, br, 1H, NH)	14.3, 14.4, 61.1, 61.3, 82.3, 90.7, 112.0, 113.3, 119.3, 123.1, 123.1, 125.0, 125.0, 130.0, 130.1, 132.5, 133.7, 134.0, 137.8, 138.0, 147.9, 147.9, 167.3, 167.5, 168.4, 169.2	3424, 3296, 2208, 1654, 1590, 1526	643 (M^+ + 1)	$C_{26}H_{22}N_6O_8S_3$	48.59 48.71	3.45 3.43	13.08 13.20	14.97 15.14

[a] Dimethyl-d_6 sulfoxide was used for ^{1}H nmr solvent. [b] Potassium bromide was used for IR.

$C_{16}H_{20}N_4O_4S_3$, which was supported by the analytical data. The same reaction tendencies were observed for the reactions with other β-enamino esters in dichloromethane. The two broad signals at 5.43-6.37 ppm and 9.17–9.60 ppm exhibited by compounds **4** may be assigned to be a free NH and a NH proton forming hydrogen bond, respectively. From the reaction with ethyl 3-amino-3-phenylpropenoate **2e** (R^1 = Ph, R^2 = Et, R^3 = H) was isolated isothiazole-5-carbonitirle derivative **8** (15% yield), analogous to 5-cyano-3-methylisothiazole-4-carboxylate reported [5]. Quantities of the reactants, reaction times, and yields of products **4** and **7** are summarized in Table 1 and the spectroscopic (^{1}H and ^{13}C nmr, ir, ms) and analytical data of **4** and **7** are summarized in Table 2.

Compounds **4j-l** were prepared albeit in low yields from compound **1b** and ethyl 3-substituted aminocrotonates **2j-l** [6] in order to obtain a single crystal. Among these, only compound **4l** gave a single crystal whose crystal structure is shown in Figure 1. Crystal and refinement parameters for compound **4l** and atomic coordinates and equivalent isotropic thermal parameters of nonhydrogen atoms of **4l** are listed in Table 3 and 4, respectively. Selected bond distances and angles of **4l** are tabulated in Table 5 and 6, respectively. The X-ray crystal structure of compound **4l** clearly indicates that the stereochemistry around the C=C double bond bearing two CN groups is *cis* and the amino groups are *cis* to the ethoxycarbonyl groups. The *cis* relationship between the amino and the ethoxycarbonyl groups is consistent with the

Table 3

Crystal and Refinement Parameters for Compound **4l**

Molecular formula	$C_{28}H_{26}Cl_2N_4O_4S_2$	Z	2
Molecular weight	617.55	ρ calc. g cm^{-3}	1.355
Temperature	293(2) K	Crystal size, mm	0.1x0.2x0.2
Wavelength	0.71070 Å	Scan type	w/2q
Crystal system	Triclinic	θ range, deg	1.78 to 20.00
Space group	P 1	m (Mo-K_a) mm^{-1}	0.392
a, Å	11.102(3)	N_b of measured reflections	2820
b, Å	12.537(12)	N_b of reflections used $F_o > 3\sigma(F_o)$	2810
c, Å	12.790(15)	N_b of refined parameters	361
α, deg	116.28(9)	R	0.2427
β, deg	98.03(5)	Rw	0.3688
γ, deg	71.55(3)	Diffractometer	Enraf-Nomius CAD-4
V, $Å^3$	1514(2)		

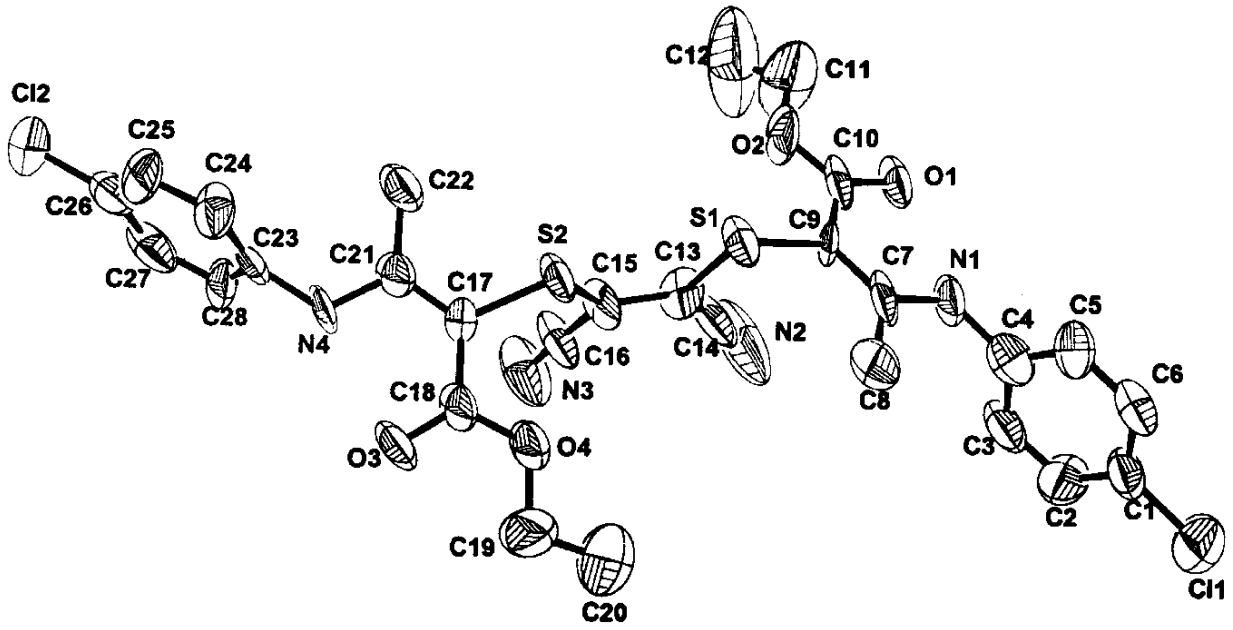


Figure 1. Molecular structure of compound **4l** with the atomic numbering scheme.

Table 4

Positional and Equivalent Isotropic Thermal Parameters of Nonhydrogen Atoms for **4l**

Atom	X	Y	Z	U_{eq} (Å^2)	Atom	X	Y	Z	U_{eq} (Å^2)
S(1)	0.4810(4)	0.2712(5)	0.0930(4)	0.064(2)	C(9)	0.3228(15)	0.3199(19)	0.0543(14)	0.052(5)
S(2)	0.7196(4)	0.2135(5)	0.2537(4)	0.062(2)	C(10)	0.2709(20)	0.4549(22)	0.0767(14)	0.065(6)
Cl(1)	-0.2174(6)	-0.0382(7)	-0.2128(6)	0.119(2)	C(11)	0.3095(28)	0.6449(23)	0.1487(31)	0.158(14)
Cl(2)	1.3204(6)	0.5076(6)	0.8154(6)	0.112(2)	C(12)	0.3518(44)	0.7125(32)	0.2323(39)	0.291(34)
O(1)	0.1590(12)	0.4988(11)	0.0567(10)	0.071(4)	C(13)	0.4638(15)	0.3090(17)	0.2403(15)	0.063(5)
O(2)	0.3528(12)	0.5163(13)	0.1208(13)	0.094(5)	C(14)	0.3415(26)	0.3657(24)	0.2905(19)	0.100(8)
O(3)	0.8522(11)	0.0608(13)	0.4706(12)	0.089(5)	C(15)	0.5673(14)	0.2945(20)	0.3153(18)	0.077(6)
O(4)	0.6959(11)	0.0460(12)	0.3393(11)	0.077(4)	C(16)	0.5484(16)	0.3354(21)	0.4353(21)	0.082(7)
N(1)	0.1297(14)	0.2757(15)	-0.0225(12)	0.075(5)	C(17)	0.8082(16)	0.1918(19)	0.3726(14)	0.061(6)
N(2)	0.2385(20)	0.4073(29)	0.3277(21)	0.173(13)	C(18)	0.7896(16)	0.0953(19)	0.0398(17)	0.069(6)
N(3)	0.5321(16)	0.3605(21)	0.5281(17)	0.118(8)	C(19)	0.6652(22)	-0.0397(25)	0.3733(26)	0.132(10)
N(4)	0.9691(13)	0.2289(15)	0.5119(13)	0.072(5)	C(20)	0.5511(28)	-0.0595(36)	0.3217(33)	0.212(18)
C(1)	-0.1181(19)	0.0532(19)	-0.1569(19)	0.071(6)	C(21)	0.8956(16)	0.2532(17)	0.4271(16)	0.058(5)
C(2)	-0.1085(21)	0.1178(21)	-0.0405(19)	0.087(7)	C(22)	0.9061(16)	0.3596(19)	0.4065(17)	0.084(7)
C(3)	-0.0242(21)	0.1856(20)	0.0033(17)	0.083(6)	C(23)	1.0569(17)	0.0297(20)	0.5813(20)	0.066(6)
C(4)	0.0417(19)	0.2017(18)	-0.0692(21)	0.068(5)	C(24)	1.1637(18)	0.2918(20)	0.5405(17)	0.080(6)
C(5)	0.0275(18)	0.1439(18)	-0.1834(18)	0.067(5)	C(25)	1.2467(16)	0.3537(21)	0.6149(22)	0.083(7)
C(6)	-0.0574(18)	0.0708(19)	-0.2290(16)	0.069(6)	C(26)	1.2162(20)	0.4302(20)	0.7327(21)	0.071(6)
C(7)	0.2529(17)	0.2403(21)	0.0050(14)	0.072(6)	C(27)	1.1118(22)	0.4282(20)	0.7665(17)	0.080(6)
C(8)	0.3032(18)	0.1037(17)	-0.0182(18)	0.088(7)	C(28)	1.0253(17)	0.3678(21)	0.6981(21)	0.077(6)

Table 5

Selected Bond Distances (Å) for **4l**

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S1	C9	1.745(16)	C9	C10	1.509(24)
S1	C13	1.750(18)	C13	C15	1.410(22)
S2	C15	1.756(17)	C17	C18	1.365(4)
S2	C17	1.770(14)	C17	C21	1.353(23)
C7	C9	1.338(23)			

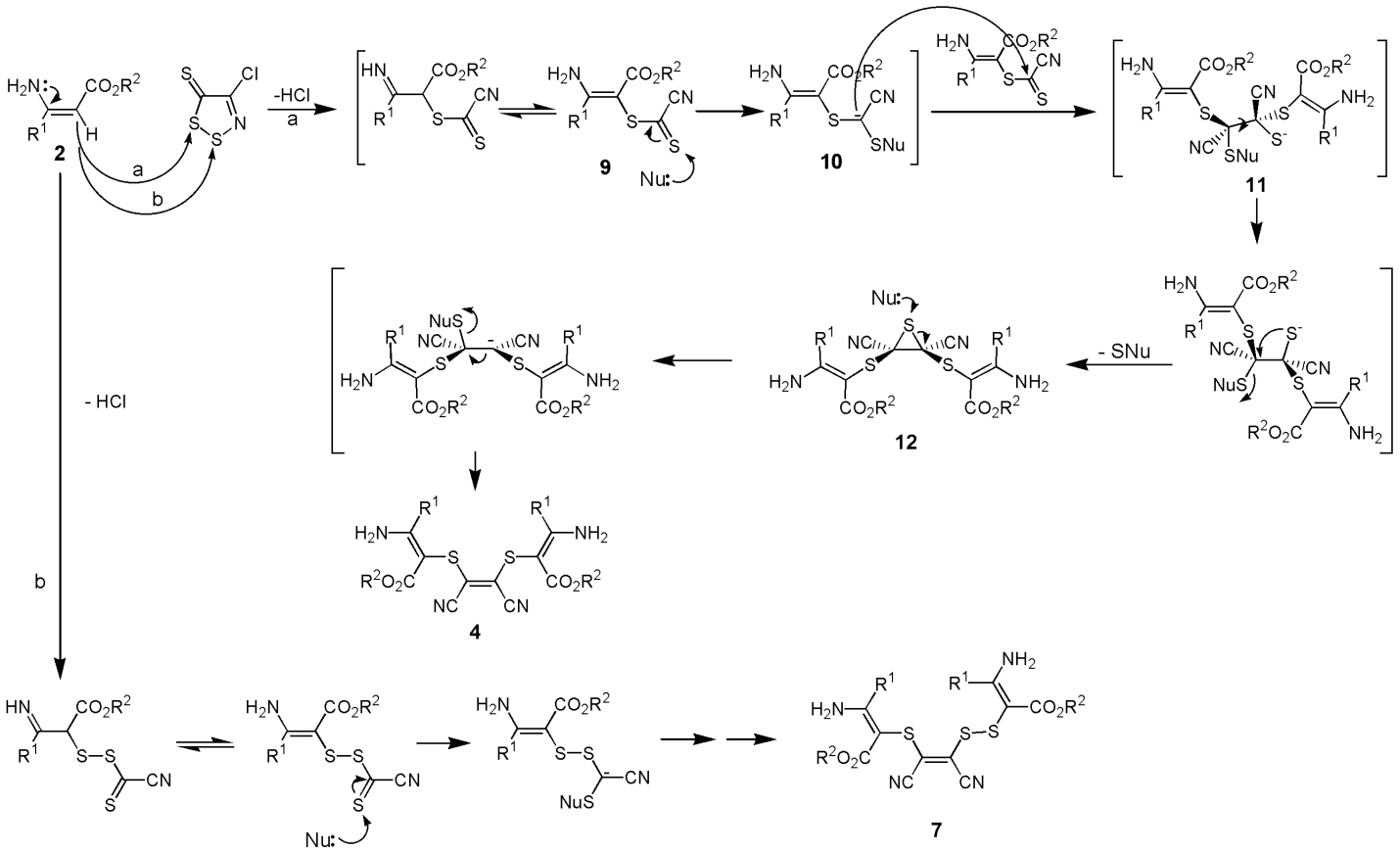
appearance of the NH proton signal so downfield at 11.87 ppm due to the formation of a hydrogen bond.

The mechanism for the formation of compounds **4** may be explained by a nucleophilic attack of the enamino carbon of compounds **2** on S-1 of the thione **1b** (path a) to give cyanoformyldithiolate **9** as an intermediate, which is subsequently attacked by nucleophile(s), presumably chloride ion, generating a carbanion **10** (Scheme 2). The resulting anion may be stabilized by electron-withdrawing

Table 6
Selected Bond Angles (deg) for **4l**

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C9	S1	C13	100.6(8)	C14	C13	C15	117.2(16)
C15	S2	C17	101.5(8)	S2	C15	C13	118.3(15)
S1	C9	C7	121.3(16)	S2	C15	C16	120.6(12)
S1	C9	C10	116.5(13)	C13	C15	C16	121.0(15)
C7	C9	C10	122.2(16)	S2	C17	C18	115.5(15)
S1	C13	C14	119.3(13)	S2	C17	C21	120.8(14)
S1	C13	C15	123.4(13)	C18	C17	C21	123.4(14)

Scheme 2



CN group. Subsequent nucleophilic attack of the carbanion **10** on another molecule of an intermediate **9** would give rise to thiolate **11**, which undergoes an intramolecular S_N2 type displacement, followed by cleavage of the C-S bond of thiirane **12**, generating a carbanion, from which *cis* products **4** are formed. An analogous mechanism was proposed for the formation of *cis*-2,3-bis(dimethylthio)-2-butenedinitrile when a mixture of sodium cyanide and carbon disulfide was treated with methyl iodide [7]. Likewise, the formation of compound **7** can be explained by the same mechanistic pathway shown by path b.

It has been found that compounds **7a** and **7e** in acetonitrile were converted to compounds **4a** (61%) and **4e** (84%), respectively, by heating at reflux. This result suggests that one can significantly increase yields of compounds **4** by the same treatment.

In summary, it has been found that treatment of 4-chloro-4*H*-1,2,3-dithiazole-5-thione **1b** with alkyl 3-alkyl (or aryl)-3-amino-2-propenoates in the presence of pyridine (2 equivalents) in dichloromethane at reflux gave *cis*-bis(2,3-dialkenylthio)-2-butenedinitriles, which may be utilized as starting materials for the synthesis of a new type of alkenylthioporphyrazines, being important in diverse areas [4].

EXPERIMENTAL

The ^1H and ^{13}C nmr spectra were recorded at 300 MHz and 75 MHz in deuteriochloroform solution containing tetramethylsilane as an internal standard, respectively; J-values are given in Hz. Infrared spectra were recorded in potassium bromide or for thin-film samples on potassium bromide plates. Mass spectra were obtained by electron impact at 70 eV. Fab mass and elemental analyses were determined by the Inter-University Center for Natural Science Research Facilities, Seoul National University. Column chromatography was performed using silica gel (Merck, 230-400 mesh, ASTM). Melting points were determined on a Fisher-johns melting point apparatus and are uncorrected. Solvents were pre-dried over sodium. 4-Chloro-5*H*-1,2,3-dithiazole-5-thione **1b** [2], methyl 3-benzylaminocrotonate **2j** [6], methyl 3-isopropylaminocrotonate **2k** [6], and methyl 3-(4-chloroanilino)crotonate **2l** [6], were prepared according to the literature procedure.

Reaction of 4-Chloro-5*H*-1,2,3-dithiazole-5-thione (**1b**) with Ethyl 3-Aminocrotonate (**2b**).

To a solution of compound **1b** (294 mg, 1.62 mmoles) in dimethyl sulfoxide (10 ml) was added amino ester **2b** (542 mg, 4.20 mmoles). The mixture was stirred for 4 days at room temperature. After addition of dichloromethane (50 ml), the mixture was washed with water (3 x 40 ml). The dichloromethane layer was dried over magnesium sulfate. Evaperation of the solvent gave a residue, which was chromatographed on a silica gel column (3 x 15 cm). Elution with *n*-hexane and a mixture of *n*-hexane and ethyl acetate (3:1) gave sulfur (6 mg, 6%), and unreacted **2b** (123 mg, 23%), respectively. Subsequent elution with the same solvent mixture (3:1) gave 3,5-diethoxycarbonyl-2,6-dimethyl-1,4-thiazine (**5**) (44 mg, 10%) [1]. Elution with the same solvent mixture (2:1) gave unknown mixtures (56 mg) and 2-amino-1-ethoxycarbonyl-1-propenyl tetrasulfide (**6**) (67 mg, 13%), which was recrystallized from dichloromethane – *n*-hexane: mp 130–132 °C; ^1H nmr (deuteriochloroform): δ 1.30 (t, 6H, J = 7.1 Hz, $2CH_3$), 2.33 (s, 6H, $2CH_3$), 4.22 (q, 4H, J = 7.1 Hz, 2 OCH_2), 5.61 (s, 2H, 2NH), 9.45 (s, 2H, 2NH); ir (potassium bromide): 3392, 3296, 1613, 1488, 1360, 1248, 1069 cm^{-1}; fab ms *m/z* 385 ($M^+ + 1$).

Anal. Calcd. for $C_{12}H_{20}N_2O_4S_4$: C, 37.48; H, 5.24; N, 7.28; S, 33.35. Found: C, 37.40; H, 5.24; N, 7.21; S, 33.50.

Continuous elution with the same solvent mixture (2:1) gave ethyl 3-amino-2-[2-(2-amino-1-ethoxycarbonylpropenyl-sulfanyl)-1,2-dicyanovinylsulfanyl]-2-butenoate (**4b**) (58 mg, 18%). Consult Table 2 for the spectroscopic and analytical data of **4b**.

General Procedure for the Reaction of Substrate **1b** with β-Enamino Esters **2** in Dichloromethane.

To a solution of thione **1b** (0.60–1.66 mmoles) in dichloromethane (5 ml) was added β-enamino ester **2** (0.69–2.45 mmoles) and pyridine (1.86–3.70 mmoles) in a sequence. The reaction mixture was heated at reflux until the spot corresponding to compound **1b** had disappeared on thin layer chromatogram (silica gel, R_f = 0.72, ethyl acetate:*n*-hexane = 1:3) except for the reaction mixture containing compounds **2a**, **2j**, **2k** and **2l**, which were stirred at room temperature. After the solvent was removed *in vacuo*, the residue was chromatographed on a silica gel (230 - 400 mesh, 3 x 15 cm). Elution with *n*-hexane and a mixture of *n*-hexane and ethyl acetate (5:1) as an eluent gave sulfur and unreacted ester **2**, respectively. Subsequent elution with the same solvent mixture (3:1) gave unknown mixture, 3-amino-2-[2-(2-amino-1-ethoxycarbonylpropenylsulfanyl)-1,2-dicyanovinylsulfanyl]-2-butenoic ethyl esters (**4**) and 3-amino-2-[2-(2-amino-1-ethoxycarbonylpropenylsulfanyl)-1,2-dicyanovinyldisulfanyl]-2-butenoic ethyl esters (**7**). Consult Table 1 for reaction conditions and yields and melting points and Table 2 for the spectroscopic and analytical data of compounds **4** and **7**.

General Procedure for Conversion of Disulfides **7** into Sulfides **4**.

A solution of compounds **7** (0.075 – 0.080 mmole) in acetonitrile (10 ml) was heated for an appropriate time at reflux until no spot corresponding to compounds **7** had observed on thin layer chromatogram (silica gel, *n*-hexane:ethyl acetate = 2:1). Removal of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (70 – 230 mesh, 3 x 10 cm). Elution with *n*-hexane gave a trace amount of sulfur. Subsequent elution with a mixture of *n*-hexane and ethyl acetate (1:1) gave compounds **4**.

In accordance with the above general procedure, heating compound **7a** (30 mg, 0.075 mmole) for 48 hours at reflux gave compound **4a** (17 mg, 61%). Similarly heating **7e** (44 mg, 0.080 mmole) for 6 hours at reflux gave **4e** (35 mg, 84%).

X-Ray Structure Determination of Compound **4l**.

The data were collected on an Enraf-Nomius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation. The structure was solved by direct methods and subsequent Fourier maps. Refinements were carried out by full-matrix least squares techniques. Non-hydrogen atoms were anisotropically refined. Atomic scattering factors were taken from International Tables for X-ray Crystallography, Vol **IV**, 1974. All calculations and drawings were performed using a Micro VAX II computer with the SDP system. Crystallographic and refinement parameters are summarized in Table 3.

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