Z isomers were separated by HPLC, using 2% ethyl acetate/hexane as eluent, to give 4.58 g of the less polar *E* ester **29** and 2.29 g of the more polar *Z* ester **29**.[15,16]

(*E*)-**29**: NMR (60 MHz, $CDCl_3$) δ 7.08 (4 H, m), 4.25 (2 H, q, J = 7 Hz), 2.34 (3 H, s), 2.04 (3 H, q, J = 0.9 Hz), 1.76 (3 H, q, J = 0.9 Hz), 1.31 (3 H, t, J = 7 Hz).

(*Z*)-**29**: NMR (60 MHz, $CDCl_3$) δ 7.08 (4 H, m), 3.88 (2 H, q, J = 7 Hz), 2.32 (3 H, s), 1.95 (3 H, br s), 1.93 (3 H, br s) 0.87 (3 H, t, J = 7 Hz).

(*EZ*)-**29**: IR (liquid film) 2940, 1730, 1515, 1450, 1370, 1255, 1140, 1100, 1060, 840 cm^{-1}.

2,3,4′-Trimethylcinnamyl Alcohol (27). The ester (*E*)-**29** (4.25 g, 19.5 mmol) dissolved in 20 mL of diethyl ether was added dropwise to a suspension of lithium aluminum hydride (0.888 g, 23.4 mmol) in 100 mL of diethyl ether at 0 °C. The mixture was stirred at 0 °C for 45 min and then quenched by successive addition of 0.9 mL of water, 0.9 mL of 15% sodium hydroxide solution, and 2.7 mL of water. The aluminum salts were filtered and washed with ether, and the combined ether layers were dried over sodium sulfate and evaporated to give 3.77 g of a yellow oil. Distillation produced 3.02 g (88%) of the alcohol **27** as a colorless oil: bp 125–30 °C (0.4 mm); NMR (60 MHz, $CDCl_3$) δ 7.05 (m, 4 H), 4.31 (br s, 2 H), 2.34 (3 H, s), 2.02 (3 H, br s), 1.69 (3 H, br s), 1.55 (1 H, br s); IR (liquid film) 3700–3125 (br), 2930, 1660, 1520, 1450, 1380, 1110, 1000, 820, 725 cm^{-1}.

Reaction of 9 with 27. Powdered potassium hydroxide (91 mg, 1.61 mmol) dissolved in 1.4 g of the allylic alcohol **27** was added dropwise to a solution of 176 mg (0.65 mmol) of hexachlorocyclopentadiene (**9**) in 1.442 g of the allylic alcohol **27** at 0 °C under a nitrogen atmosphere. The reaction mixture was warmed to 25 °C and stirred for 21 h, poured onto 50 mL of ice water, and extracted with dichloromethane. The combined organic extracts were washed with brine, dried over sodium sulfate, and evaporated to give 3.91 g of a yellow oil which was chromatographed on silica gel, using 3% ethyl acetate/hexane as eluent. This produced only recovered starting material.

Acknowledgment. We thank Professor F. A. L. Anet for helpful discussions. The Bruker WP-200 NMR spectrometer was purchased with funds provided by a major instrument grant from NSF.

Registry No. 8 (keto form), 80516-08-1; 8 (hemiketal form), 80516-09-2; **9**, 77-47-4; **12**, 52144-62-4; **13**, 80516-10-5; **16**, 80516-11-6; **17**, 80516-12-7; **18**, 80516-13-8; **19** (keto form), 80516-14-9; **19** (hemiketal form), 80516-15-0; **20**, 34139-34-9; **22**, 122-00-9; **23**, 42107-37-9; **24**, 80516-16-1; **25**, 80516-17-2; **26**, 80516-18-3; (*E*)-**27**, 34716-99-9; **28**, 3699-66-9; (*E*)-**29**, 61712-12-7; (*Z*)-**29**, 61712-22-9; allyl alcohol, 107-18-6; dimethylallyl alcohol, 556-82-1.

S,N Double Rearrangement. 2.[1] X-ray Crystal Structures of Rearranged Products

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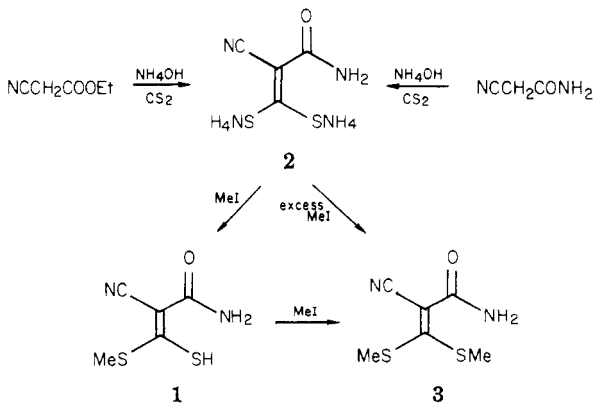
Condensation of 2-cyano-3-mercapto-3-(methylthio)acrylamide (**1**) with benzoic acid in the presence of polyphosphate ester gave 5-carbamoyl-4-(methylthio)-2-phenyl-1,3-oxazine-6-thione (**6**), which, on treatment with boiling ethanol, was easily converted into 5-carbamoyl-4-(methylthio)-2-phenyl-1,3-thiazin-6-one (**9**). Reduction of **9** with $NaBH_4$ gave its 2,3-dihydro derivative **10**. The structures of **6**, **9**, and **10** were determined by single-crystal X-ray diffraction. A reaction mechanism of this novel S,N double rearrangement is briefly discussed.

In the course of the syntheses of 1,3-thiazines and related compounds, we found an interesting condensation reaction which involved a novel rearrangement. Thus, 2-cyano-3-mercapto-3-(methylthio)acrylamide (**1**) reacted with benzoic acid in the presence of polyphosphate ester (PPE)[2] to give 5-carbamoyl-4-(methylthio)-2-phenyl-1,3-thiazin-6-one (**9**).[3] The structures of **9** and its 2,3-dihydro derivative **10** were unequivocally determined by routine single-crystal X-ray analyses. This novel condensation reaction was termed "S,N double rearrangement" and was reported in our preliminary communication.[1] Further investigation led to the isolation of a key intermediate **6**. Its X-ray structural study showed that **6** was a S,N double rearranged product, 5-carbamoyl-4-(methylthio)-2-phenyl-1,3-oxazine-6-thione. We present here more detailed results of this rearrangement and discuss the reaction mechanisms.

Results and Discussion

Structure of 1. Starting material **1** was prepared by the reaction of ethyl cyanoacetate or cyanoacetamide with carbon disulfide in the presence of ammonia, followed by monomethylation using 1 equiv of methyl iodide. In this

Scheme I



† Faculty of Science.
‡ Analytical Center.

(1) A preliminary account of some of this work has been published: M. Yokoyama, M. Nakamura, T. Imamoto, and K. Yamaguchi, *J. Chem. Soc., Chem. Commun.*, 560 (1981).
(2) W. Pollmann and G. Schramm, *Biochem. Biophys. Acta*, **80**, 1 (1964).

0022-3263/82/1947-1090$01.25/0

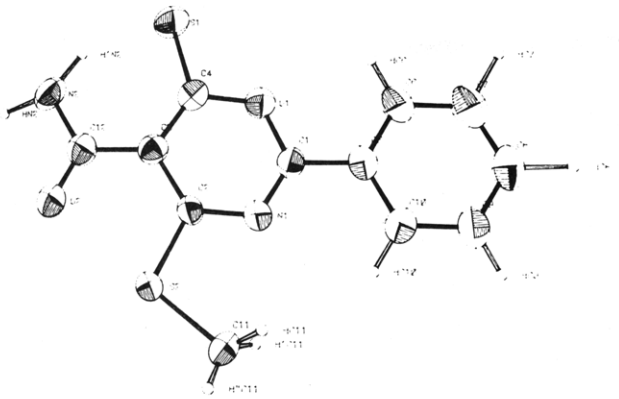


Figure 1. ORTEP diagram of **6** showing 50% probability ellipsoids for all nonhydrogen atoms.

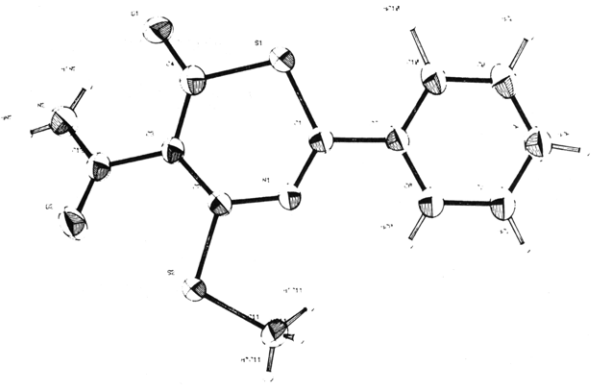


Figure 2. ORTEP diagram of **9** showing 50% probability ellipsoids for all nonhydrogen atoms.

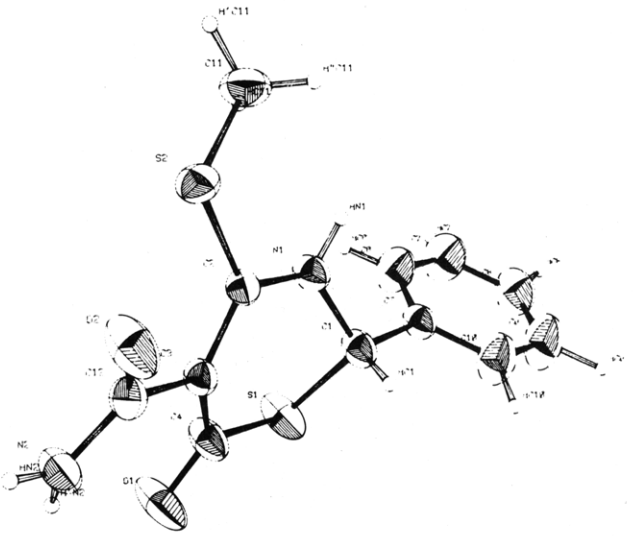


Figure 3. ORTEP diagram of **10** showing 50% probability ellipsoids for all nonhydrogen atoms.

process, an intermediate, bis(ammoniothio)-2-cyanoacrylamide (**2**), could be isolated. Treatment of **2** with a large excess methyl iodide gave bis(methylthio)-2-cyanoacrylamide **3**,[4] which could also be prepared from the reaction of **1** with methyl iodide (see Scheme I).

The structural proof of **1** was based on elemental analyses and spectroscopic data. The IR spectrum revealed the presence of amino (3400, 3200, and 3100 cm^{-1}), conjugated cyano (2200 cm^{-1}), and carbonyl (1650 cm^{-1}) groups. The NMR spectrum showed the presence of a mercapto (br, δ 16.2),[5] an amino (br, δ 8.0), and a methylthio (s, δ 2.6) group. The mass spectrum showed a molecular ion (m/e 174).

Furthermore, the structure of **1** is unequivocal judging from the fact that **1** reacted with benzaldehyde in the presence of dilute H_2SO_4 to afford 5-cyano-6-(methylthio)-2-phenyl-2,3-dihydro-1,3-thiazin-4-one (**4**), which was then converted to 5-carbamoyl-6-(methylthio)-2-phenyl-2,3-dihydro-1,3-thiazin-4-one (**5**) by acid hydrolysis (see Scheme II). The structural proof of **4** and **5** was also based on elemental analyses and spectroscopic evidence, especially mass data; the mass spectra of **4** and **5** exhibited parent ion peaks at m/e 262 and 280 and characteristic fragment peaks at m/e 219 $(M - CONH)^+$ and 237 $(M - CONH)^+$, respectively.

Reaction of 1 with Benzoic Acid in the Presence of PPE. Compound **1** was allowed to react with benzoic acid in refluxing chloroform in the presence of PPE to give 5-carbamoyl-4-(methylthio)-2-phenyl-1,3-oxazine-6-thione (**6**, yield 57%), 5-carbamoyl-4-(methylthio)-2-phenyl-1,3-thiazin-6-one (**9**, yield 4%), 5-cyano-4-(methylthio)-2-phenyl-1,3-thiazin-6-one (**11**, yield 4%), and *N*-benzoyl-3-mercapto-3-(methylthio)-2-cyanoacrylamide (**8**) as a minor product. Compound **6** could be quantitatively converted to **9** by treatment in a protic solvent such as methanol, ethanol, or propanol. This transformation could not proceed in an aprotic solvent such as THF, chloroform, ethyl acetate, Me_2SO, or acetone. The reduction of **9** using $NaBH_4$ in ethanol afforded 5-carbamoyl-4-(methylthio)-2-phenyl-2,3-dihydro-1,3-thiazin-6-one (**10**) quantitatively. The structures of **6**, **9**, and **10** were determined by a single-crystal X-ray diffraction study. Figures 1–3 illustrate their ORTEP drawings. Crystal data and data collection details are summarized in Table I (supplementary material). Tables II–VII (supplementary material) show bond lengths and bond angles of compounds **6**, **9**, and **10**.

From these results, it was concluded that a hitherto unknown S,N double rearrangement took place in the condensation step of **1** with benzoic acid in the presence of PPE.

Reaction of 1 with Benzoic Anhydride in the Presence of PPE. When **1** was reacted with benzoic anhydride in chloroform at reflux in the presence of PPE, 5-cyano-4-(methylthio)-2-phenyl-1,3-oxazine-6-thione (**7**) was isolated in 35% yield. Subsequent treatment of **7** with ethanol afforded **11**, which was then reduced with $NaBH_4$ to give 5-cyano-4-(methylthio)-2-phenyl-2,3-dihydro-1,3-thiazin-6-one (**12**). This compound **12** was isomeric with **4**. Compound **11** was also prepared from dehydration of **9** by utilizing PPE. Similarly, **12** was also obtained from **10**.

Reaction of 1 with Benzoyl Chloride in the Presence of Pyridine. Compound **1** was allowed to react with benzoyl chloride in the presence of pyridine to give *N*-benzoyl-3-(methylthio)-3-(pyridiniothio)-2-cyanoacrylamide (**13**) and 5-cyano-6-(methylthio)-2-phenyl-1,3-thiazin-4-one (**14**) in 57% and 34% yields, respectively. On treatment with dilute HCl, **13** was converted quantitatively into **8**, which was then treated with refluxing chloroform in the presence of PPE to give **14**. Treatment of **14** with $NaBH_4$ afforded **4**. Compounds **14** and **11** are isomeric with each other.

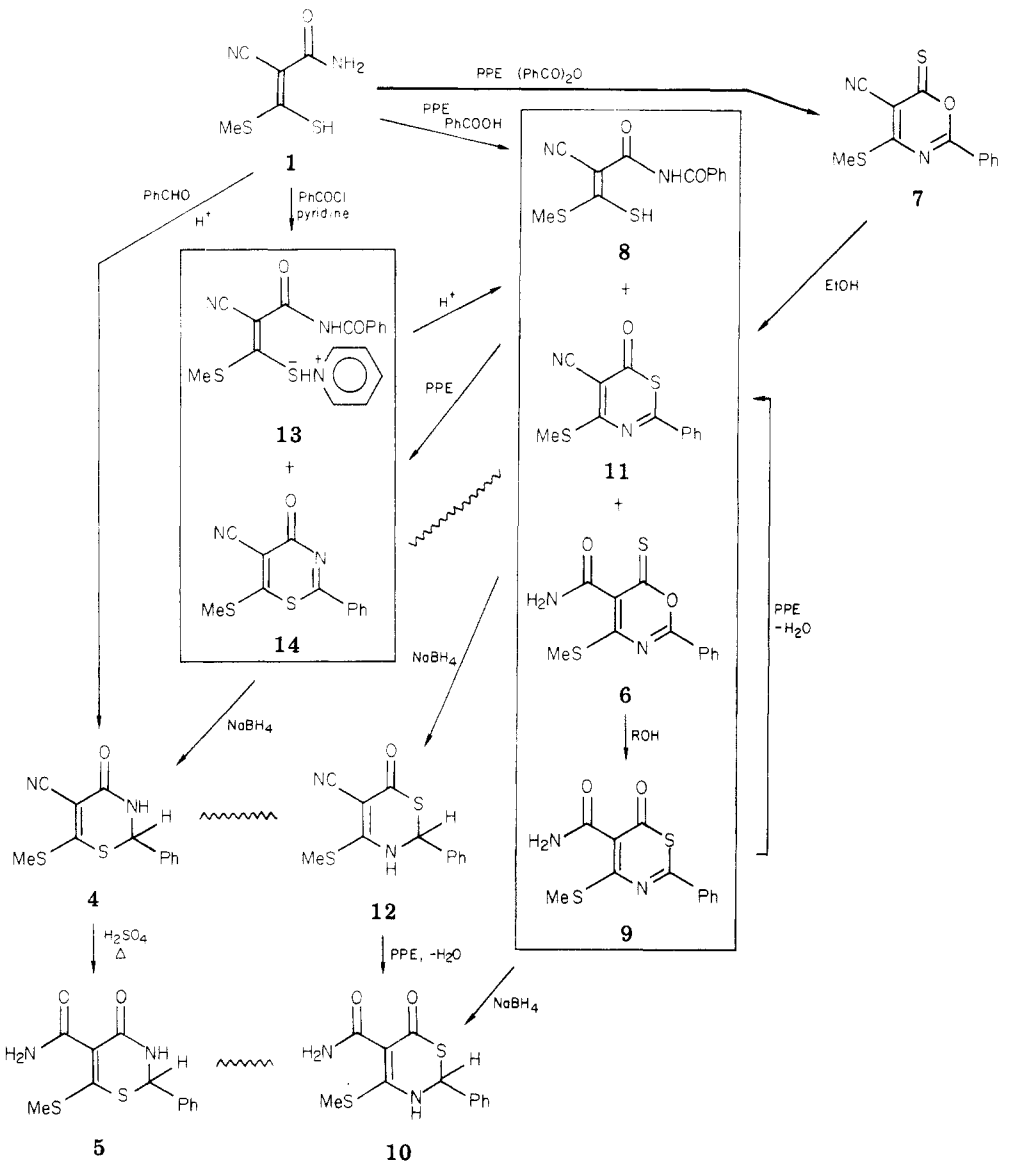
(3) M. Yokoyama, Y. Sawachi, and T. Isso, *J. Org. Chem.*, **38**, 802 (1973). Compound **9** was assigned the structure of 5-carbamoyl-6-(methylthio)-2-phenyl-1,3-thiazin-4-one mainly on the basis of spectroscopic data.

(4) T. Takeshima, M. Yokoyama, N. Fukada, and M. Akano, *J. Org. Chem.*, **35**, 2438 (1970).

(5) An extreme downfield shift of the proton of the mercapto group may be due to an intramolecular hydrogen bonding.

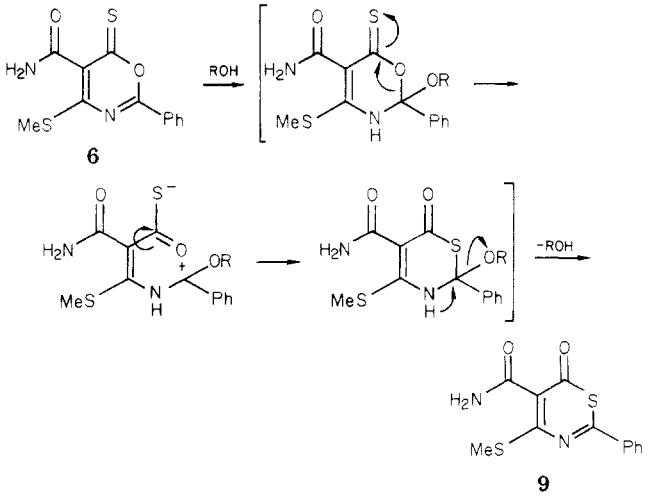
(6) A report describing the preparation of 1,3-oxazine-6-thiones: J. W. Lown and K. Matsumoto, *Can. J. Chem.*, **50**, 584 (1972).

Scheme II[a]



[a] A⁓B shows that A and B are S,N-interchanged position isomers.

Scheme II shows the interconversion of compounds mentioned above. The mechanism of transformation **6** → **9** or **7** → **11** can be shown as follows. The driving force



of this rearrangement is considered to be the conversion of a 1,3-oxazine ring to a more stable 1,3-thiazine one.

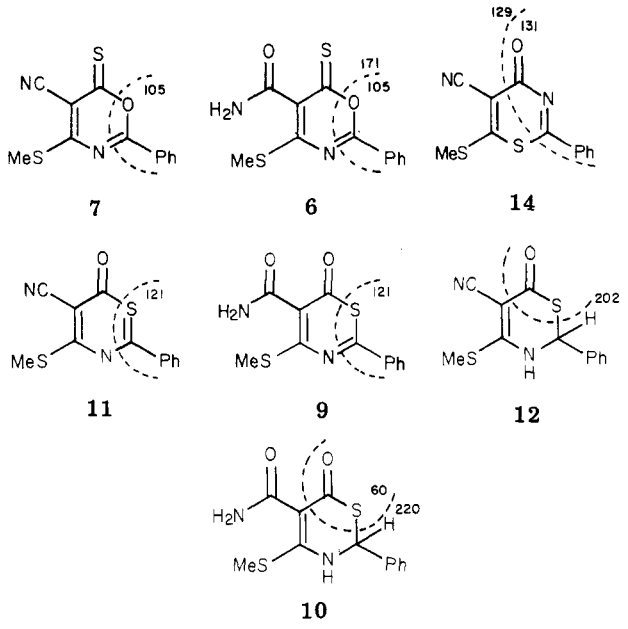
Structures of 7, 11, 12, and 14. The structures of compounds synthesized were assigned on the basis of their spectroscopic evidence, especially characteristic mass fragment peaks illustrated in Chart I and IR data, together with elemental analyses. The IR spectrum of **11** showed carbonyl absorption at 1630 cm^{-1}, while no carbonyl one appeared in that of **7**.

Mechanism of S,N Double Rearrangement. It is interesting to consider on the sequence from **1** to **7**. The overall process can be explained by assuming a few intermediates (see Scheme III). The carbamoyl group of **1** attacks benzoic anhydride activated by PPE to generate an intermediate **16**. The subsequent cyclization by intramolecular attack of mercapto group generates an unstable thiete derivative **17**. This intermediate immediately rearranges to **18**, which, in turn, is cyclized by dehydration to form **7**. In the case of formation of **6** using benzoic acid, the cyano group of **1** is considered to be hydrated in the process of **16** → **17** → **18**.

The following result can also support this mechanism. That is, the reaction of **8** with benzoic acid utilizing PPE afforded neither **6** nor **7**, therefore **8** is not an intermediate in this rearrangement.

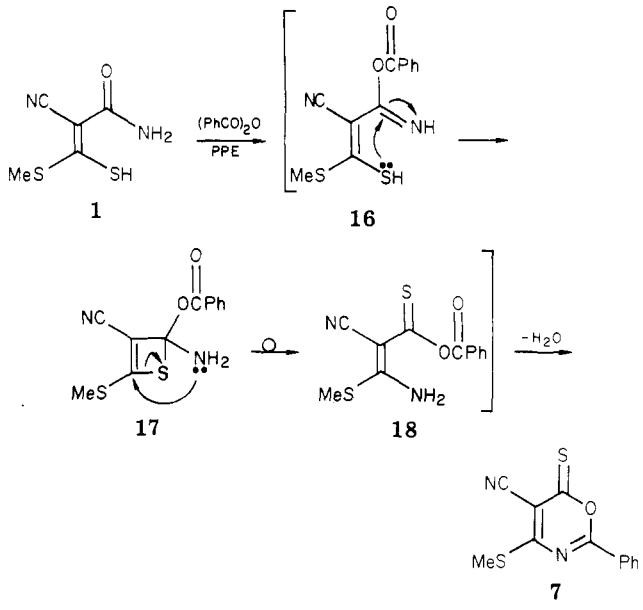
We are now examining the scope and limitation of this

Chart I[a]



[a] The numbers on the dashed lines are *m/e* fragmentation values.

Scheme III



rearrangement, and further interesting properties of 1,3-oxazine-6-thiones such as **6** and **7**, because its chemistry has been scarcely touched.[6]

Experimental Section

Microanalyses were performed with a Perkin-Elmer 240 elemental analyser at the Analytical Center of Chiba University. IR, UV, mass, ^{1}H NMR, and ^{13}C NMR spectra were measured with Japan Spectroscopic Co. DS-403G, Hitachi EPS-3T, and RMU-6MC instruments and Japan Electron Optics Lab. Co. C-60HL and FX-100 instruments, respectively. Silica gel used in column chromatography was Wakogel C-200, and silica gel used for thin-layer chromatography (TLC) was Wakogel B-5F.

2-Cyano-3-mercapto-3-(methylthio)acrylamide (1). Compound **1**[4,7] was prepared by the following modified method. A mixture of ethyl cyanoacetate (120 g, 1.1 mol), carbon disulfide (161 g, 2.1 mol), and 360 mL of aqueous ammonia (28%) was stirred at room temperature for 8 h. The crude product was collected and recrystallized from water–acetone to give light yellow prisims [bis(ammoniothio)-2-cyanoacrylamide (**2**)]: yield 83 g (40%); mp 147–148 °C dec.

To a mixture of **2** (47 g, 270 mmol), EtOH (400 mL), and H_2O (700 mL) was added methyl iodide (16.8 mL, 270 mmol) under cooling with stirring. The mixture was stirred for 2 h and then added the dilute HCl (ca. 300 mL) to give white crystals, which were recrystallized from EtOH–H_2O without heating to afford 26 g (62% yield) of **1**: mp 149–150 °C dec; IR (KBr) 3400, 3280, 3180 (NH_2), 2200 (CN), 1650 (CO) cm^{-1}; NMR (acetone-d_6) δ 16.2 (br, 1, SH), 8.0 (br, 2, NH_2), 2.6 (s, 3, CH_3); mass spectrum, *m/e* 174 (M^+). Anal. Calcd for $C_5H_6N_2OS_2$: C, 34.48; H, 3.44; N, 16.08; S, 36.81. Found: C, 34.45; H, 3.43; N, 16.03; S, 36.79.

5-Cyano-6-(methylthio)-2-phenyl-2,3-dihydro-1,3-thiazin-4-one (4).[7] A mixture of benzaldehyde (8 g, 75 mmol), **1** (3 g, 17.2 mmol), 20% H_2SO_4 (10 mL), and methanol (35 mL) was refluxed for 10 min. The crude material was collected, washed with ethanol, dried, and recrystallized from acetic acid to give colorless prisms in quantitative yield: mp 225–226 °C; IR (KBr) 3290 (NH), 2950 (CH), 2200 (CN), 1660 (CO), 1608 (C=C or NH) cm^{-1}; NMR (Me_2SO-d_6) δ 9.1 (d, 1, NH), 7.5 (s, 5, Ph), 6.4 (d, 1, CH), 2.65 (s, 3, CH_3); UV max (99% EtOH) 235 nm (sh), 280 (ϵ 13 000), 336 (15 000); mass spectrum, *m/e* 262 (M^+), 215 (M – SCH_3), 185 (M – Ph), 157 (M – NHCHPh). Anal. Calcd for $C_{12}H_{10}N_2OS_2$: C, 54.96; H, 3.81; N, 10.68; S, 24.45. Found: C, 54.81; H, 3.91; N, 10.57; S, 24.25.

5-Carbamoyl-6-(methylthio)-2-phenyl-2,3-dihydro-1,3-thiazin-4-one (5). Compound **4** (0.4 g, 1.5 mmol) was heated with concentrated H_2SO_4 (2 mL) until red-brown turbidity appeared. The reaction mixture was poured into ice–water to give a light yellow material. Recrystallization from AcOH–H_2O gave 0.34 g (yield 80%) of light yellow needles: mp 205–206 °C; IR (KBr) 3350, 3150 (NH), 3000 (Ph), 2850 (CH), 1640 (CO) cm^{-1}; NMR (Me_2SO-d_6) δ 8.9 (d, 1, NH), 8.2 (br, 1, NH_2), 7.5 (m, 5, Ph), 7.3 (br, 1, NH_2), 6.1 (d, 1, CH), 2.3 (s, 3, CH_3); UV max (99% EtOH) 238 nm (sh), 278 (ϵ 5600), 332 (7000); mass spectrum, *m/e* 280 (M^+), 237 (M – CONH), 233 (M – SCH_3), 175 (M – PhCHNH), 132 (PhCNHCO), 105 (PhCHNH), 104 (PhC=NH), 77 (Ph). Anal. Calcd for $C_{12}H_{12}N_2O_2S_2$: C, 51.43; H, 4.28; N, 9.99; S, 22.88. Found: C, 51.40; H, 4.28; N, 9.96; S, 22.90.

5-Carbamoyl-4-(methylthio)-2-phenyl-1,3-oxazine-6-thione (6). A mixture of **1** (0.5 g, 2.9 mmol), benzoic acid (0.35 g, 2.9 mmol), PPE (1 g), and chloroform (12 ml) was refluxed for 30 min. By addition of ethanol to the reaction mixture, an orange product (**6**; 0.46 g, yield 57%) was obtained. Recrystallization from chloroform gave orange needles: mp 205–206 °C; IR (KBr) 3300, 3130 (NH_2), 1660 (CO), 1600 (NH_2) cm^{-1}; NMR (Me_2SO-d_6) δ 8.3 (m, 2, Ph), 8.1 (br, 1, NH_2), 7.8 (m, 4, NH_2, Ph), 2.8 (s, 3, CH_3); UV max (99% EtOH) 232 nm (ϵ 8900), 275 (sh), 309 (19 000), 405 (6900); mass spectrum, *m/e* 278.0197 (M^+), 263 (M – CH_3), 231 (M – SCH_3), 105 (PhCO), 77 (Ph). Anal. Calcd for $C_{12}H_{10}N_2O_2S_2$: C, 51.80; H, 3.59; N, 10.06; S, 23.04. Found: C, 51.82; H, 3.60; N, 10.06; S, 23.10.

5-Cyano-4-(methylthio)-2-phenyl-1,3-thiazin-6-one (11). The mother liquor separated from **6** was rotary evaporated to give red oil, which was then triturated with ethanol–H_2O to form 0.1 g of yellow precipitates. From this material, **11** (30 mg, yield 4%) and **9** (30 mg, yield 4%) were separated by silica gel chromatography with benzene and successive ethyl acetate as eluants. Namely, **11** was isolated from the benzene eluant and **9** from the ethyl acetate one. Compound **11** was recrystallized from chloroform to give yellow needles: mp 206–207 °C; IR (KBr) 2210 (CN), 1630 (CO) cm^{-1}; NMR (Me_2SO-d_6) δ 8.2 (m, 2, Ph), 7.8 (m, 3, Ph), 2.8 (s, 3, SCH_3); UV max (99% EtOH) 233 nm (sh), 273 (ϵ 11 000), 310 (8300), 386 (4500); mass spectrum, *m/e* 260 (M^+), 245 (M – CH_3), 232 (M – CO), 153 (M – COS – SCH_3), 121 (PhCS). Anal. Calcd for $C_{12}H_8N_2OS_2$: C, 55.38; H, 3.07; N, 10.76; S, 24.64. Found: C, 55.36; H, 3.05; N, 10.79; S, 24.61.

5-Carbamoyl-4-(methylthio)-2-phenyl-1,3-thiazin-6-one (9). Compound **9** was isolated as yellow needles [mp 222–223 °C (from AcOH)] by the same method as described in the preparation of **11**: IR (KBr) 3380, 3160 (NH_2), 1660 (sh, CO), 1636 (CO) cm^{-1}; NMR (Me_2SO-d_6) δ 8.1 (m, 2, Ph), 7.8 (m, 3, Ph), 8.0 (br, 1, NH_2), 7.65 (br, 1, NH_2), 2.7 (s, 3, SCH_3); UV max (99% EtOH) 235 nm (sh), 277 (ϵ 16 000), 340 (7500); mass spectrum, *m/e* 278.0191 (M^+), 263 (M – CH_3), 250 (M – CO), 121 (PhCS). Anal. Calcd for

(7) M. Yokoyama, *Bull. Chem. Soc. Jpn.*, **44**, 1610 (1971).

$C_{12}H_{10}N_2O_2S_2$: C, 51.80; H, 3.59; N, 10.06; S, 23.04. Found: C, 51.82; H, 3.56; N, 10.10; S, 22.98.

Conversion of 6 to 9. A mixture of **6** (200 mg, 0.7 mmol) and methanol, ethanol, or propanol (20 mL) was refluxed for 2 h. Evaporation of the solvent gave **9** (200 mg).

In the previous work[1,3] we isolated only **9** as orange plates or yellow needles because all of **6** was changed to **9** on the recrystallization from AcOH–H_2O or heating in ethanol.

***N*-Benzoyl-3-mercapto-3-(methylthio)-2-cyanoacrylamide (8).** The filtrate separated from **9** and **11** was rotary evaporated to give a small amount of **8**, which was recrystallized from benzene to afford colorless needles: mp 138–139 °C; IR (KBr) 2200 (CN), 1650 (CO) cm^{-1}; NMR ($CDCl_3$) δ 15.8 (br, 1, SH), 11.7 (br, 1, NH), 8.2 (m, 2 Ph), 7.8 (m, 3, Ph), 2.8 (s, 3, CH_3); mass spectrum, *m/e* 278 (M^+), 231 (M – SCH_3), 147 (CO – N – COPh), 121 ($PhCONH_2$), 105 (PhCO), 77 (Ph). Anal. Calcd for $C_{12}H_{10}N_2O_2S_2$: C, 51.80; H, 3.59; N, 10.06; S, 23.04. Found: C, 51.78; H, 3.46; N, 10.00; S, 22.96.

5-Cyano-4-(methylthio)-2-phenyl-1,3-oxazine-6-thione (7). A mixture of **1** (0.2 g, 1.2 mmol), benzoic anhydride (0.27 g, 1.2 mmol), PPE (2 mL), and chloroform (2 mL) was refluxed for 1 h. The resulting red precipitates were collected; 0.1 g (yield 35%). Recrystallization from benzene gave red needles: mp 196–198 °C dec; IR (KBr) 2920 (Ph), 2210 (CN) cm^{-1}; mass spectrum, *m/e* 260 (M^+), 245 (M – CH_3), 105 (PhCO), 77 (Ph). Anal. Calcd for $C_{12}H_8N_2OS_2$: C, 55.38; H, 3.07; N, 10.76; S, 24.64. Found: C, 55.30; H, 3.12; N, 10.74; S, 24.62. Upon treatment with ethanol at room temperature for 2 h, **7** was converted into **11** quantitatively.

***N*-Benzoyl-3-(methylthio)-3-(pyridiniothio)-2-cyanoacrylamide (13).** A mixture of **1** (2 g, 11.4 mmol), benzoyl chloride (1.3 mL, 11.4 mmol), pyridine (2.8 mL), and chloroform (20 mL) was refluxed for 40 min to give 2.35 g of colorless precipitates (yield 57%), which was recrystallized from ethanol to afford colorless needles: mp 171–173 °C; IR (KBr) 3050 (Ph), 2800 (pyridinium salt), 2180 (CN) cm^{-1}; NMR (Me_2SO-d_6) δ 14.3 (br, 1, SH), 10.4 (br, 1, NH), 9.0 (d, 2, pyridine), 8.7 (d, 1, pyridine), 8.1 (m, 4, Ph, pyridine), 7.7 (m, 3, Ph), 2.6 (s, 3, CH_3). From the above filtrate, was isolated 1 g of **14**. Compound **13** was treated with 4 N HCl to yield **8** in 85% yield.

5-Cyano-6-(methylthio)-2-phenyl-1,3-thiazin-4-one (14). A mixture of **1** (1 g, 5.7 mmol), benzoyl chloride (2 mL, 17.3 mmol), pyridine (1.4 mL), and chloroform (20 mL) was refluxed for 2 h. To the reaction mixture was added EtOH–H_2O (20 mL) to give 1.47 g (yield 98%) of red crystals, which was recrystallized from benzene with activated charcoal to give light yellow needles: mp 176–178 °C; IR (KBr) 3070 (Ph), 2990, 2900 (CH), 2210 (CN), 1630 (CO) cm^{-1}; NMR (Me_2SO-d_6) δ 8.2 (m, 2, Ph), 7.8 (m, 3 Ph), 2.9 (s, 3, CH_3); mass spectrum, *m/e* 260 (M^+), 157 (M – PhCN), 131 (PhCNCO), 110 (M – PhCN – SCH_3), 103 (PhCN), 76 (Ph); UV max (99% EtOH) 274 nm (ϵ 35600), 315 (14700). Anal. Calcd for $C_{12}H_8N_2OS_2$: C, 55.38; H, 3.07; N, 10.76; S, 24.64. Found: C, 55.36; H, 3.07; N, 10.77; S, 24.68.

5-Cyano-4-(methylthio)-2-phenyl-2,3-dihydro-1,3-thiazin-6-one (12). A mixture of **11** (112 mg, 0.43 mmol), $NaBH_4$ (58 mg, 1.53 mmol), and ethanol (10 mL) was stirred at room temperature for 2 h. To the reaction mixture was added 4 N HCl solution until the evolution of H_2 gas ceased. The precipitates were filtered off, and in turn the solvent was rotary evaporated to give an viscous solution, which was treated with ether to form 112 mg of **12**. Recrystallization from AcOH–H_2O gave colorless needles: mp 167–168 °C; IR (KBr) 3330 (NH), 3030 (Ph), 2210 (CN), 1600 (CO) cm^{-1}; NMR (Me_2SO-d_6) δ 9.9 (br, 1, NH), 7.5 (s, 5, Ph), 6.5 (s, 1, CH), 2.8 (s, 3, CH_3); UV max (99% EtOH) 228 nm (ϵ 17000), 260 (9200), 327 (9900); mass spectrum, *m/e* 262 (M^+), 247 (M – CH_3), 202 (M – COS), 155 (M – SCH_3 – COS), 122 (PhCHS). Anal. Calcd for $C_{12}H_{10}N_2OS_2$: C, 54.96; H, 3.81; N, 10.68; S, 24.45. Found: C, 54.93; H, 3.83; N, 10.70; S, 24.48.

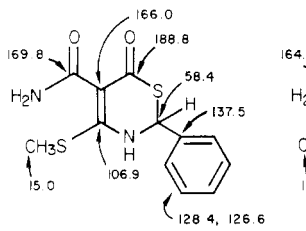
5-Carbamoyl-4-(methylthio)-2-phenyl-2,3-dihydro-1,3-thiazin-6-one (10). The reduction of **9** was carried out in the same way as described in the preparation of **12** (yield 68%). Recrystallization from AcOH–H_2O gave colorless prisms: mp 183–184 °C dec; IR (KBr) 3380, 3280, 3150 (NH), 1645 (CO) cm^{-1}; NMR (Me_2SO-d_6) δ 8.8 (br, 1, NH), 7.9 (br, 1 NH_2), 7.4 (s, 5, Ph), 6.9 (br, 1, NH_2), 6.3 (d, 1, CH), 2.4 (s, 3, CH_3); UV max (99% EtOH) 243 nm (ϵ 11000), 270 (sh), 331 (8400); mass spectrum, *m/e* 280 (M^+), 265 (M – CH_3), 220 (M – COS), 203 (M – Ph), 173 (M – SCH_3 – COS), 156 (M – Ph – SCH_3), 121 (PhCS), 60 (COS). Anal. Calcd for $C_{12}H_{12}N_2O_2S_2$: C, 51.43; H, 4.28; N, 9.99; S, 22.88. Found: C, 51.46; H, 4.30; N, 9.96; S, 22.83.

Conversion of 8 into 14. A mixture of **8** (150 mg, 0.54 mmol), PPE (0.5 mL), and chloroform (3.5 mL) was refluxed for 6 h. The reaction mixture was rotary evaporated and triturated with ethanol to give 102 mg of **14** (yield 73%).

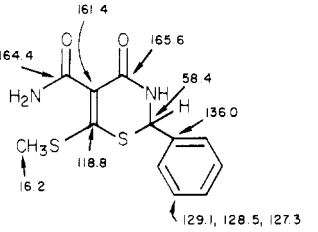
Conversion of 9 into 11. This transformation was carried out in 91% yield by the same method as described above.

Conversion of 10 into 12. This reaction was confirmed by TLC method.

The ^{13}C NMR values for **5** and **10** in Me_2SO-d_6 are given in δ units below.



10



5

X-ray Crystallographic Analysis of 6. A large, well-shaped monoclinic crystal of **6** was obtained by slow evaporation of a dimethyl acetylenedicarboxylate–chloroform solution: $C_{12}H_{10}N_2O_2S_2$; space group $P2_1/c$-C_{2h}^5; a = 5.049 (3), b = 8.008 (1), c = 33.128 (8) Å; β = 112.34°; Z = 4. Lattice constants and intensity data for **6** were measured by using graphite-monochromated Cu Kα radiation on a Rigaku AFC-5 diffractometer. A total of 1990 unique reflections with $F_o > 2\sigma(F_o)$ were obtained by using the ω–2 scanning method with a 2θ scan speed of 4°/min to 2θ = 145°. The structure was solved by the RASA-II system (Rigaku Corp.) on the basis of the direct method and refined to a final R value of 0.093. The program was executed on a 16 bit/word minicomputer with a 64K-byte 1C memory and 10M bytes on magnetic disk. Further crystallographic details can be found in the supplementary material described in the paragraph at the end of this paper.

X-ray Crystallographic Analysis of 9. A large, well-shaped monoclinic crystal was obtained by slow evaporation of a chloroform–ethanol solution: $C_{12}H_{10}N_2O_2S_2$; space group $P2_1/c$-C_{2h}^5; a = 7.688 (3), b = 5.156 (3), c = 31.473 (8) Å; β = 105.52 (3)°; Z = 4. Analytical conditions were as described for **6**.

X-ray Crystallographic Analysis of 10. A large, well-shaped orthorhombic crystal was obtained by slow evaporation of an acetone–methanol solution: $C_{12}H_{12}N_2O_2S_2$; space group $Pbcn$-D_{2h}^{14}; a = 13.218 (3), b = 9.562 (3), c = 20.220 (10) Å; Z = 8. Lattice constants and intensity data for **10** were measured by using graphite-monochromated Mo Kα radiation on a Rigaku AFC-5 diffractometer. A total of 2598 unique reflections with $F_o > 2\sigma(F_o)$ were obtained by using the ω–2 scanning method with a 2θ scan speed of 2°/min to 2θ = 60°. The structure was solved by the RASA-II system (Rigaku Corp.) on the basis of the direct method and refined to a final R value of 0.062.

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Registry No. **1**, 37614-61-2; **2**, 24571-59-3; **4**, 33050-23-6; **5**, 79402-45-2; **6**, 80532-87-2; **7**, 80532-88-3; **8**, 80532-89-4; **9**, 79402-44-1; **10**, 79402-43-0; **11**, 80532-90-7; **12**, 80532-91-8; **13**, 80532-92-9; **14**, 80532-93-0; benzaldehyde, 100-52-7; benzoic acid, 65-85-0; benzoic anhydride, 93-97-0; benzoyl chloride, 98-88-4.

Supplementary Material Available: Tables of atomic coordinates and details of data collection (Table I), bond lengths (Tables II, IV, and VI), and bond angles (Tables III, V, and VII) for compounds **6**, **9**, and **10** (10 pages). Ordering information is given on any current masthead page.