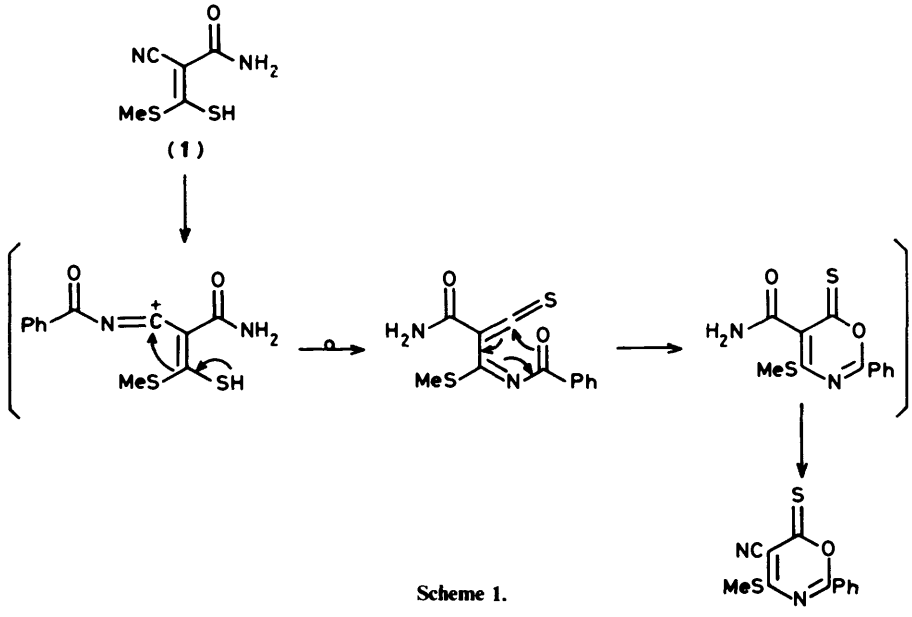
Heteroatom Rearrangements. S,N, O,N, and N,N Double Rearrangements. *X*-Ray Molecular Structure of 5-Cyano-6-methylthio-2,3-diphenylpyrimidin-4(3*H*)-one

Masataka Yokoyama,*[a] Hidekatsu Hatanaka,[a] Atsuhi Sasaki,[a] Tadashi Shiraishi,[a] Katsushi Kumata,[a] Kayoko Sakamoto,[a] and Koreharu Ogata[b]
[a] Department of Chemistry, Faculty of Science, and [b] Analytical Center, Chiba University, Yayoi-cho, Chiba City, 260, Japan

New heteroatom rearrangements are reported; 'S,N, O,N, and N,N double rearrangements' take place when acrylonitriles, substituted at C-3 by two heteroatom groups (MeS or MeSe, and SH, OH, or NHPh), condense with aromatic carboxylic acids in the presence of dehydrating agents such as PPE, PPSE, phosphoryl trichloride, and propylphosphonic acid cyclic anhydride. The key step of this reaction is the acylation of the cyano group of the acrylonitrile, followed by transfer of the heteroatom group (SMe or SeMe).

A study of the synthesis of 1,3-thiazin-4-ones led to our discovery of the 'S,N double rearrangement.' This novel reaction, involving a simultaneous interchange of sulphur and nitrogen atoms, was observed when 2-cyano-3-mercapto-3-(methylthio)acrylamide (**1**) condensed with benzoic acid in the presence of polyphosphate ester (PPE).[1,2]

The elucidation of the reaction mechanism by means of ^{13}C labelling and crossover experiments revealed that (i) benzoic acid is activated by PPE to generate a benzoyl-cation-like species, (ii) this species is responsible for the benzoylation of cyano group in compound (**1**), (iii) a methylthio group in compound (**1**) transfers to the carbon atom of the benzoylated cyano group, (iv) a 1,3-oxazine ring is formed by cyclization, and (v) a carbamoyl group is dehydrated (see Scheme 1).[3]

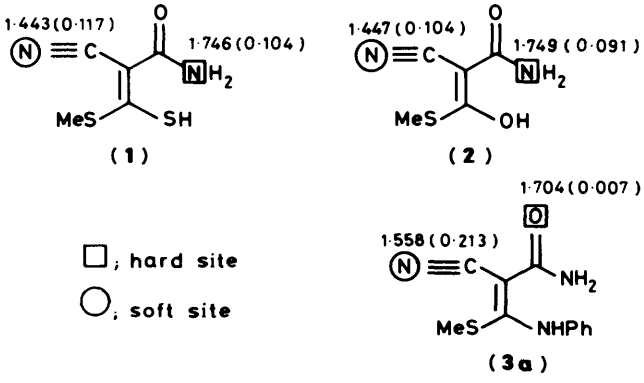


Scheme 1.

It is a key step of this reaction that in 'soft benzoyl cation' generated by PPE attacks exclusively on the nitrogen atom of the cyano group, which is considered to be a 'soft nucleophilic site' in amide (**1**).†

As an extension of the S,N double rearrangement, the use of 2-cyano-3-hydroxy-3-(methylthio)acrylamide (**2**) [*O*-analogue of (**1**)] and 3-anilino-2-cyano-3-(methylthio)acrylamide (**3a**) [*N*-analogue of (**1**)] under the same conditions could give rise to the first examples of 'O,N double rearrangement' and '*N,N* double rearrangement,' respectively.[4] Further, we found that *S*-methyl cyanothioacetates (**4**), 3-anilino-3-methyl-

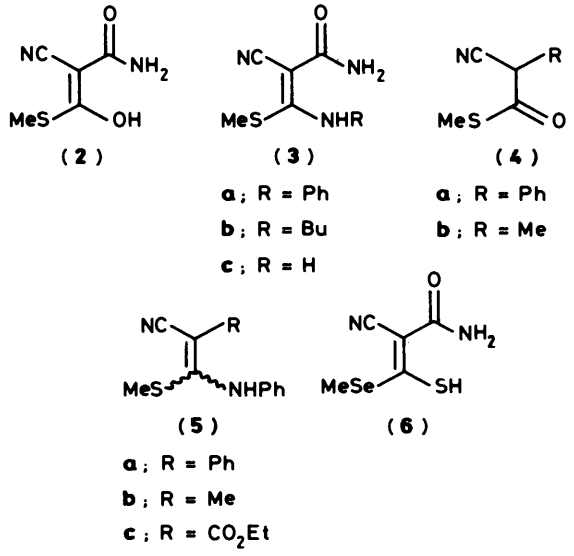
† HMO Calculations show the following electron density for compounds (**1**), (**2**), and (**3a**). The values in parentheses show the HOMO electron density.



thioacrylonitriles (**5**), and 2-cyano-3-mercapto-3-(methylseleno)acrylamide (**6**) [*Se*-analogue of (**1**)] could also undergo the present heteroatom rearrangement. Herein we describe the synthesis of compounds (**2**)—(**6**) and the structure determination of their heteroatom-rearranged products.

Results and Discussion

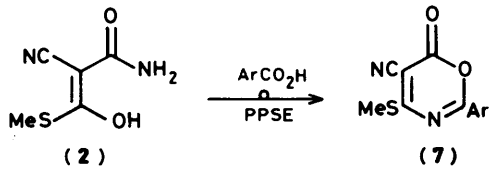
O,N Double Rearrangement.—Compound (**2**) was prepared from the reaction of *SS*-dimethyl dithiocarbonate with cyano-



acetamide and was allowed to react with benzoic acid in the presence of PPE in the usual way.[2] An expected compound, (**7a**), 5-cyano-4-methylthio-2-phenyl-1,3-oxazin-6-one, was obtained in fair yield (50%). The reaction was then carried out under more drastic conditions (120 °C) using polyphosphoric trimethylsilyl ester (PPSE)[5] which could be employed without decomposition at high temperature. Thus a satisfactory result was obtained (see Table 1). The starting compound (**2**) exists in the *E*-form due to the hydrogen bond between the carbamoyl and hydroxy groups (see Experimental section).

The structure of the products (**7**) was determined from the

Table 1. Preparation of oxazinones (**7**)

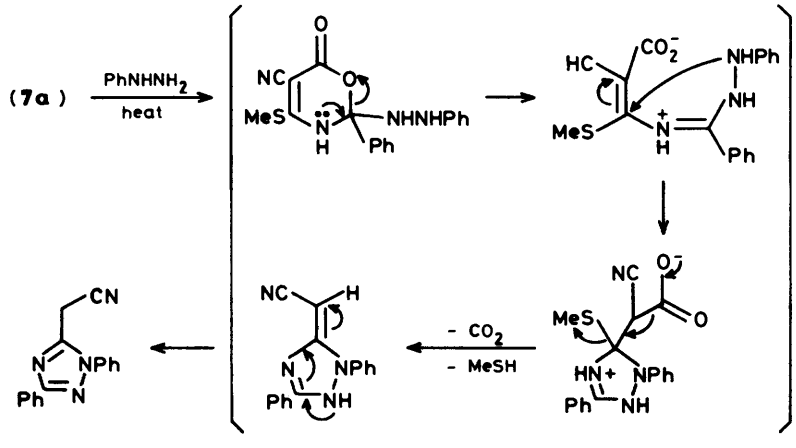


Cmpd.	Ar	Yield (%)	Cmpd.	Ar	Yield (%)
(**7a**)	phenyl	77	(**7d**)	2-naphthyl	68
(**7b**)	4-methoxyphenyl	79	(**7e**)	4-nitrophenyl	56
(**7c**)	4-chlorophenyl	74	(**7f**)	2-furyl	49

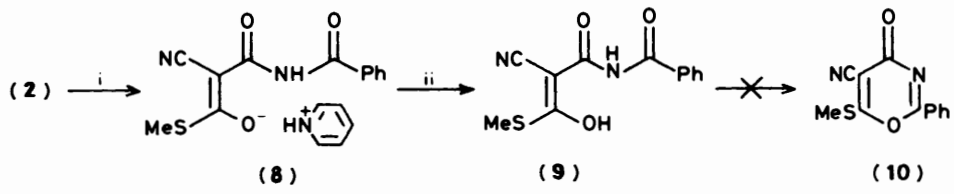
results of the following conversion reaction. Compound (**7a**) was allowed to react with phenylhydrazine in chloroform to give 5-cyanomethyl-1,3-diphenyl-1*H*-1,2,4-triazole[6] with loss of carbon dioxide and methanethiol (see Scheme 2). Further, the presence of i.r. stretching bands (1 730—1 750 cm^{-1}) characteristic of lactones also support the assigned structures (**7**).

On the other hand, compound (**2**) reacted with benzoyl chloride in the presence of pyridine to give the pyridinium salt (**8**) of *N*-benzoyl-2-cyano-3-hydroxy-3-(methylthio)acrylamide, which was, in turn, converted into *N*-benzoyl-2-cyano-3-hydroxy-3-(methylthio)acrylamide (**9**) on treatment with mineral acid (Scheme 3). Attempted ring closure of compound (**9**) to give the 1,3-oxazin-4-one derivative (**10**) was unsuccessful. However, it is noteworthy that compound (**9**), when treated with PPSE, gave rise to the oxazinone (**7a**). This fact suggests that compound (**9**) does not give compound (**10**) directly by dehydrative ring-closure, but instead gives (**7a**) *via* a dehydrated species (**11**) and then a rearranged species (**12**) because of the weak nucleophilicity of the hydroxy group (Scheme 4).

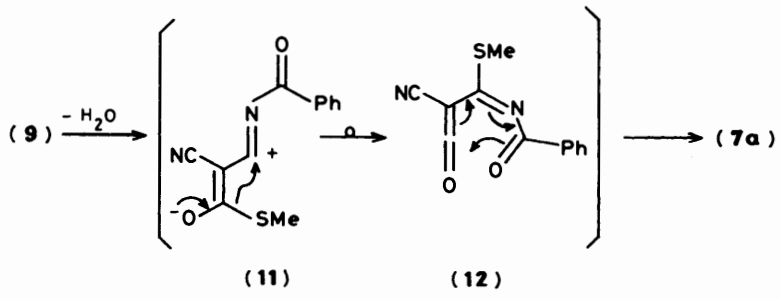
Next, compounds (**4**) were synthesized from the reaction of the corresponding nitriles with *SS*-dimethyl dithiocarbonate. The structures of compounds (**4**) were assigned as *S*-methyl cyanothioacetates based on spectral evidence (see Experimental section). Compounds (**4**) condensed with benzoic acid under the same conditions as described for the formation of compounds (**7**) to give the corresponding O,N rearranged products (**13**) in low yields. The results are shown in Table 2.



Scheme 2.

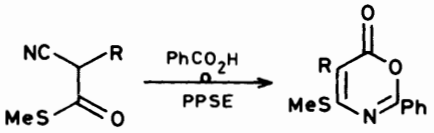


Scheme 3. *Reagents:* i, PhCOCl, pyridine; ii, H^+



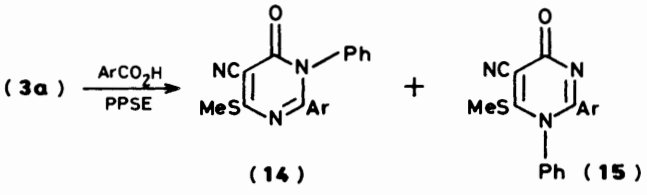
Scheme 4.

Table 2. Preparation of oxazinones (13) from thioesters (4)



(4)	(13)	R	Yield (%)
(4a)	(13a)	Ph	29
(4b)	(13b)	Me	36

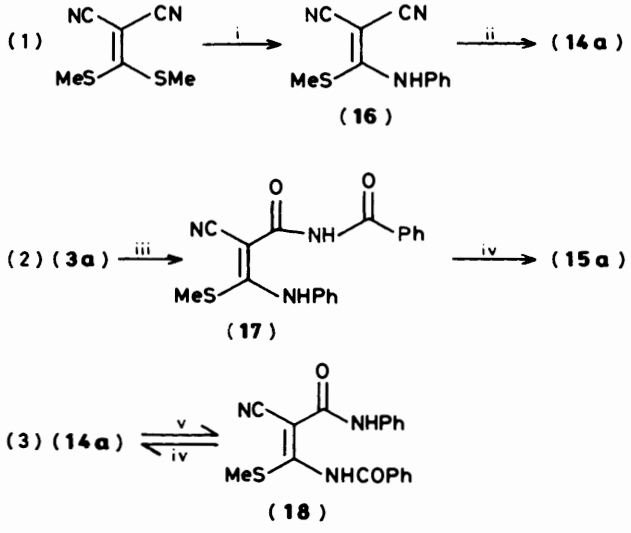
Table 3. Preparation of pyrimidinones (14) and (15)



		Yield (%)		
(14), (15)	Ar	(14)	(15)	Total
(14a), (15a)	phenyl	49	11	60
(14b), (15b)	4-nitrophenyl	54	24	78
(14c), (15c)	4-chlorophenyl	47	38	85

In the present reaction the use of phosphoryl trichloride and propylphosphonic acid cyclic anhydride[7] as condensation reagents gave similar results (see Experimental section).

N,N Double Rearrangement.—Compound (**3a**), 3-anilino-2-cyano-3-(methylthio)acrylamide, was prepared by the reaction of 2-cyano-3,3-bis(methylthio)acrylamide[8] with aniline. The condensation of compound (**3a**) with benzoic acid in the presence of PPSE at 150—160 °C gave a rearranged product (**14a**), 5-cyano-6-methylthio-2,3-diphenylpyrimidin-4(3*H*)-one, together with an unrearranged product (**15a**), 5-cyano-6-methylthio-1,2-diphenylpyrimidin-4(1*H*)-one. In a similar manner, some substituted benzoic acids were converted into the corresponding pyrimidinones (**14**) and (**15**). The results are summarized in Table 3.



Scheme 5. *Reagents:* i, $PhNH_2$; ii, $PhCO_2H$, PPSE; iii, NaH, then PhCOCl; iv, PPSE; v, 10% NaOH

The structures of products (**14**) and (**15**) were assigned from the results of the following conversion reactions (Scheme 5).

Therefore, the conversion of 3-anilino-2-cyano-3-methylthioacrylonitrile (**16**) into compound (**14a**) suggests that the pyrimidinone (**14a**) has a rearranged structure; dehydrative ring-closure of 3-anilino-*N*-benzoyl-2-cyano-3-(methylthio)-acrylamide (**17**) gave an unrearranged product (**15a**); alkaline hydrolysis of (**14a**) afforded 3-benzamido-2-cyano-3-methyl-

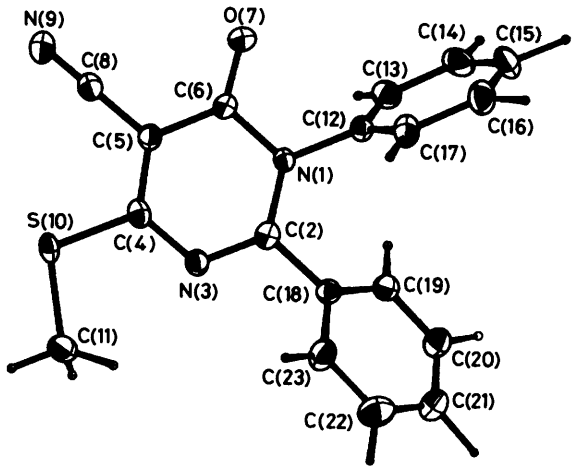
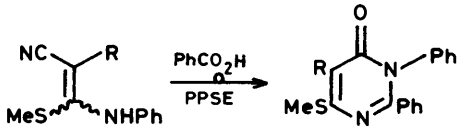


Figure. ORTEP diagram of compound (**14a**) showing 50% probability ellipsoids for all non-hydrogen atoms

thio-*N*-phenylacrylamide (**18**) [a positional isomer of (**17**)], which, in turn, could be recyclized to the pyrimidinone (**14a**) in the presence of PPSE. The structure of compound (**14a**) was determined unequivocally by a single-crystal *X*-ray diffraction study,* and the Figure illustrates its ORTEP drawing. Detailed crystallographic results are given in the Experimental section.

Monitoring of the reaction of compound (**3a**) with benzoic acid by t.l.c. revealed that the pyrimidinone (**14a**) was produced *via* a dehydrated compound (**16**). Therefore, the present reaction is considered to form compound (**16**) and (**17**) competitively (Scheme 6).

Table 4. Preparation of pyrimidinones (**19**) from nitriles (**5**)



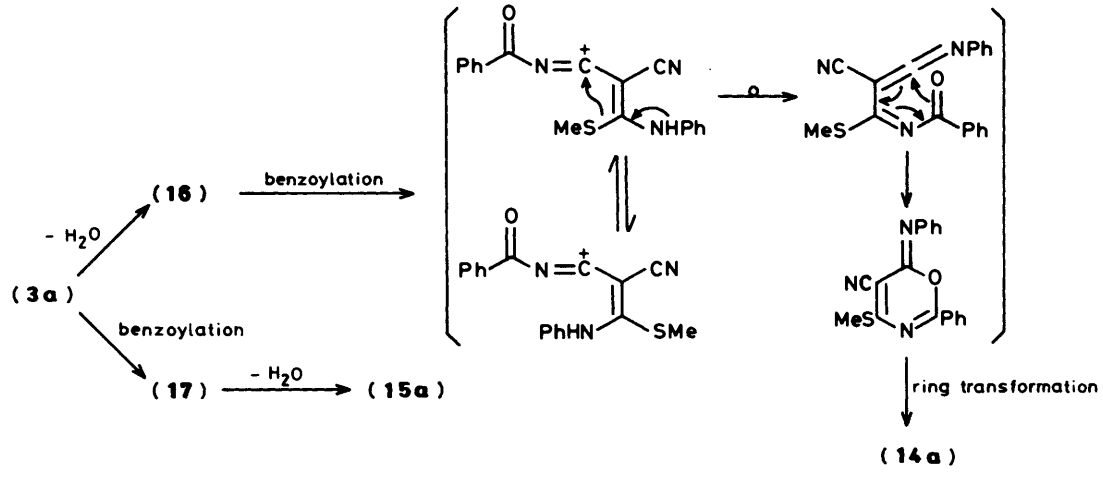
(**5**) (**19**)

(5)	(19)	R	Yield (%)
(**5a**)	(**19a**)	Ph	70
(**5b**)	(**19b**)	Me	76
(**5c**)	(**19c**)	CO_2Et	70

pared by the same method as described for the preparation of (**3a**) by using, respectively, n-butylamine and ammonium benzoate in place of aniline. However, compounds (**3b**) and (**3c**) did not undergo the present cyclization reaction, perhaps because of the strong basicity of the butylamino and amino groups.

Continuing our search for the limitations of the present reaction, we intended to apply this reaction of compounds (**5**), which were prepared (as *E*:*Z* mixtures) from the reaction of the corresponding nitriles with phenyl isothiocyanate. When nitriles (**5**) condensed with benzoic acid under the same conditions as mentioned above, the corresponding pyrimidines (**19**) were obtained in moderate yield. The results are shown in Table 4.

In this reaction three dehydrating agents containing phosphorus were employed. A phosphoryl trichloride solution containing amide (**3a**) and benzoic acid was refluxed for 6 h to give only the pyrimidinone (**14a**) in 43% yield, with no isomer (**15a**).



Scheme 6.

Although it is not clear why N,N double rearrangement is accompanied by a side-reaction forming the unrearranged product (**15a**), the result may be explained on the hypothesis that the hydrogen bond between the carbamoyl and imino groups increases the nucleophilicity of the carbamoyl group [compare the chemical-shift values of amino protons in the carbonyl groups: δ_H 6.42 in (**3a**); 7.5 in (**2**); 8.0 in (**1**)].

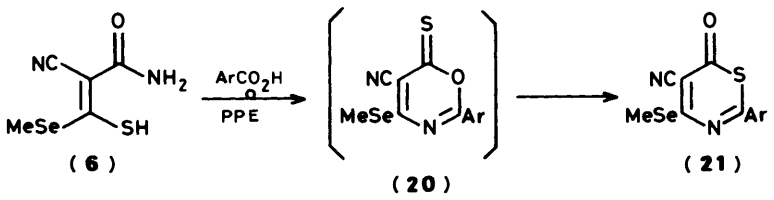
Next, 3-butylamino-2-cyano-3-(methylthio)acrylamide (**3b**) and 3-amino-2-cyano-3-(methylthio)acrylamide (**3c**) were prepared by the same method as described for the preparation of (**3a**) by using, respectively, n-butylamine and ammonium benzoate in place of aniline. However, compounds (**3b**) and (**3c**) did not undergo the present cyclization reaction, perhaps because of the strong basicity of the butylamino and amino groups.

The use of diethylphosphoryl cyanide (DEPC)[9] gave an unsatisfactory result; 3-anilino-3-methylthioacrylonitrile† (33%) and recovered (**3a**) (63%). The reaction of amide (**3a**) with benzoic acid in the presence of propylphosphonic acid cyclic anhydride afforded many products; (**14a**) (64%), (**15a**) (8%), (**16**) (20%), and (**18**) (trace).

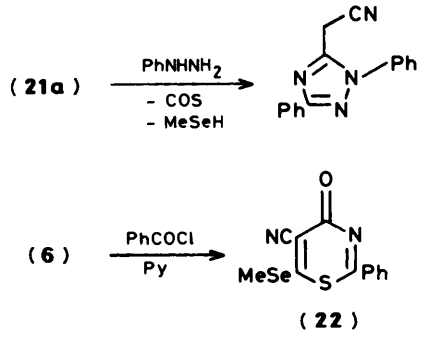
* Large, well shaped monoclinic crystals of compound (**14a**) were obtained by slow evaporation of an ethanolic solution.

† We tentatively assigned the structure of this compound as 3-anilino-3-methylthioacrylonitrile from the following data; white powder, m.p. 73 °C (from EtOH); $\nu_{max.}$(KBr) 3 280vs, 3 040m, 2 900m, 2 200vs, 1 540vs, and 1 510vs cm^{-1}; *m/z* 190 (M^+) (Found: C, 63.0; H, 5.3; N, 14.55. Calc. for $C_{10}H_{10}N_2S$: C, 63.13; H, 5.30; N, 14.72%).

Table 5. Preparation of thiazinones (21)



(21)	Ar	Yield (%)
(21a)	phenyl	66
(21b)	2-naphthyl	72
(21c)	4-methoxyphenyl	53

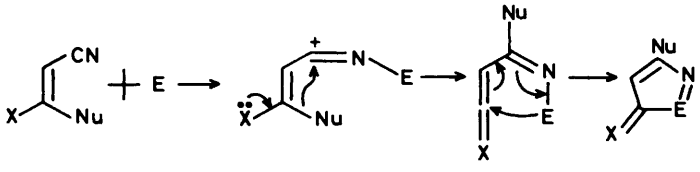


S,N *Double Rearrangement using* Se *Analogue of* (1).—A key step of the present heteroatom rearrangement is the transfer of the methylthio group. In order to examine the transfer of a methylseleno group, we prepared compound (6), which was derived from the reaction of cyanoacetamide with *SeSe*-dimethyl thiodiselenocarbonate[11] in the presence of sodium hydride. Compound (6) condensed with benzoic acid under the same conditions as described in the N,N double rearrangement methaneselenol by the same mechanism as shown in Scheme 2. In the case of the condensation with benzoic acid, compound (20a) was isolated and could be quantitatively converted into its isomer (21a) with refluxing ethanol owing to the difference of stability in the heteroaromatics. Further, an unrearranged product (22), 5-cyano-6-methylseleno-2-phenyl-1,3-thiazin-4-one, was prepared by reaction of the acrylamide (6) with benzoyl chloride in the presence of pyridine.

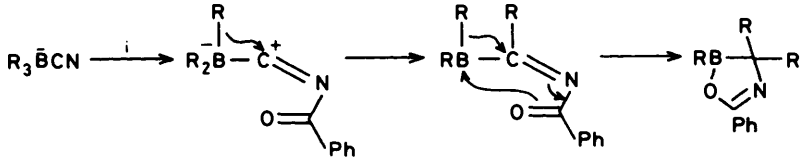
In conclusion, heteroatom rearrangements such as S,N, O,N, and N,N double rearrangements, take place when acrylonitriles, substituted at C-3 with two heteroatom groups (MeS or MeSe, and SH, OH, or NHPh), condense with aromatic carboxylic acids in the presence of dehydrating agents such as PPE, PPSE, $POCl_3$, and propylphosphonic acid cyclic anhydride. The present reaction can be summarized by Scheme 7 according to A. I. Meyers.[11]

The characteristic feature of our reaction is the transfer of the heteroatom (S or Se) shown as Nu. A similar reaction has been observed in organoboron chemistry (Scheme 8).[12]

The extension of this reaction to aliphatic carboxylic acids is under investigation in our laboratory.



Scheme 7. E, Electrophilic site; Nu, nucleophilic site



Scheme 8. *Reagent:* i, PhCOCl

section to give 5-cyano-4-methylseleno-2-phenyl-1,3-thiazin-6-one (21a) *via* an intermediate compound (20a), 5-cyano-4-methylseleno-2-phenyl-1,3-oxazine-6-thione. Some substituted benzoic acids were converted into the corresponding thiazinones (21). The results are summarized in Table 5.

The structure of compound (21a) was assigned from the isolation of 5-cyanomethyl-1,3-diphenyl-1*H*-1,2,4-triazole by reaction of (21a) with phenylhydrazine in the usual way. The triazole can be formed with loss of carbonyl sulphide and

Experimental

Microanalyses were performed with a Perkin-Elmer 240 elemental analyser at the Analytical Center of Chiba University. I.r. spectra were recorded on a Hitachi 215 spectrometer. ^1H N.m.r. spectra were determined with Japan Electron Optics Lab. (JEOL) JNM-FX-270, MH-100, and C-60 HL spectrometers. ^{13}C N.m.r. spectra were recorded with a JEOL JNM-FX-270 spectrometer. Chemical shifts are given in p.p.m. downfield from $(CH_3)_4Si$ as internal standard. U.v. spectra

were measured with a Hitachi EPS-3T spectrophotometer. Mass spectra were measured on a Hitachi M-60 spectrometer at an ionizing energy of 70 eV. Silica gel used in column chromatography was Wakogel C-200, and silica gel used for t.l.c. was Wakogel B-5F. Special grade phosphorus pentaoxide was purchased from Wako Pure Chemical Industries Ltd. Benzene and chloroform were purified by standard procedures, and tetrahydrofuran (THF) was distilled from benzophenone ketyl. Compound (**1**) was prepared by our previous method.[3]

2-*Cyano*-3-*hydroxy*-3-(*methylthio*)*acrylamide* (**2**).—To a mixture of sodium hydride (60% oil dispersion; 12 g, 300 ml) (free from oil) and dry THF (150 ml) were added successively cyanoacetamide (6.3 g, 75 mmol), copper(I) iodide (7.2 g, 37.5 mmol), and *SS*-dimethyl dithiocarbonate[13] (9.16 g, 75 mmol). The mixture was stirred at room temperature for 40 h. Then, a mixture of sodium hydride (2 g, 50 mmol), *SS*-dimethyl dithiocarbonate (2.44 g, 20 mmol), and dry THF (30 ml) was added to the reaction mixture. After being refluxed for 3 h, the mixture was quenched with water, washed with benzene, and filtered through Celite. The filtrate was acidified with dil. HCl and extracted with ethyl acetate. The extract was evaporated under reduced pressure to give a yellow material (10 g). Recrystallization from chloroform gave the *title compound* (**2**) as white prisms (9.3 g, 78%), m.p. > 340 °C (Found: C, 37.85; H, 3.8; N, 17.7. $C_5H_6N_2O_2S$ requires C, 37.97; H, 3.82; N, 17.71%); $\nu_{max.}$(KBr) 3 310br, 3 160vs, 2 200s, and 1 680s cm^{-1}; δ_H (60 MHz; $CDCl_3$–CD_3COCD_3) 7.5 (3 H, br, NH_2 and OH) and 2.4 (3 H, s, SMe).

3-*Anilino*-2-*cyano*-3-(*methylthio*)*acrylamide* (**3a**).—A mixture of 2-cyano-3,3-bis(methylthio)acrylamide[8] (3.8 g, 20 mmol), aniline (2 ml, 22 mmol), and ethanol (40 ml) was refluxed overnight. The white crystals which formed were collected, washed with ethanol, and recrystallized from ethanol to give the *title compound* (**3a**) as white needles (4.6 g, 99%), m.p. 147—149 °C (Found: C, 56.6; H, 4.8; N, 17.9. $C_{11}H_{11}N_3OS$ requires C, 56.63; H, 4.75; N, 18.01%); $\nu_{max.}$(KBr) 3 450s, 3 390vs, 3 300s, 3 240s, 3 170vs, 2 200vs, and 1 650vs cm^{-1}; δ_H (60 MHz; $CDCl_3$–CD_3COCD_3) 12.6 (1 H, br, NH), 7.4 (5 H, s, Ph), 6.42 (2 H, br, NH_2), and 2.2 (3 H, s, SMe); *m/z* 233 (M^+).

3-*Butylamino*-2-*cyano*-3-(*methylthio*)*acrylamide* (**3b**).—A mixture of 2-cyano-3,3-bis(methylthio)acrylamide (1.8 g, 10 mmol), n-butylamine (1 ml, 11 mmol), and ethanol (20 ml) was worked up in a similar manner to that described above. The white crystals produced were recrystallized from ethanol to give the title compound (**3b**) as white needles (2.1 g, 98%), m.p. 81—83 °C; $\nu_{max.}$(KBr) 3 350s, 3 180s, 2 950, 2 920w, 2 200s, 1 660vs, 1 600vs, and 1 570vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 10.9 (1 H, br, NH), 5.95 (2 H, br, NH_2), 3.55 (2 H, m, $NHCH_2$), 2.65 (3 H, s, SMe), 1.5 (4 H, m, CH_2CH_2), and 1.0 (3 H, m, Me); *m/z* 213 (M^+).

3-*Amino*-2-*cyano*-3-(*methylthio*)*acrylamide* (**3c**).—A mixture of 2-cyano-3,3-bis(methylthio)acrylamide (0.95 g, 5 mmol), ammonium benzoate (0.82 g, 6 mmol), and ethanol (10 ml) was worked up in a similar manner to that described above. The product was recrystallized from ethanol to give the title compound (**3c**) as white needles (0.6 g, 71%), m.p. 200—201 °C; $\nu_{max.}$(KBr) 3 440s, 3 340vs, 3 260s, 3 100s, 2 200vs, 1 650s, and 1 600vs cm^{-1}; δ_H (60 MHz; $CDCl_3$–CD_3SOCD_3) 8—9 (2 H, br, NH_2), 6.57 (2 H, br, $CONH_2$), and 2.5 (3 H, s, SMe); *m/z* 157 (M^+).

5-*Cyano*-4-*methylthio*-2-*phenyl*-1,3-*oxazin*-6-*one* (**7a**).—A 30 ml two-necked round-bottom flask, equipped with a reflux condenser and a Teflon-coated magnetic bar, was dried *in vacuo* and then flushed with argon. To this flask were added sequentially phosphorus pentaoxide (2 g, 7 mmol), hexamethyldisiloxane (4 ml, 20 mmol), and dry chloroform (10 ml). The mixture was heated at reflux for 0.5 h under argon until the solution was clear, and then evaporated under reduced pressure to remove most of the solvent. To the resultant liquid were added benzoic acid (249 mg, 2 mmol) and the amide (**2**) (317 mg, 2 mmol). The mixture was stirred and heated at 120 °C for 2 h, and then quenched with water. The orange crystals produced were collected, washed with ethanol, and recrystallized from benzene to give the *title oxazinone* (**7a**) as orange prisms (376 mg, 77%), m.p. 195—196 °C (Found: C, 58.9; H, 3.3; N, 11.5. $C_{12}H_8N_2O_2S$ requires C, 59.0; H, 3.30; N, 11.47%); $\nu_{max.}$(KBr) 3 050w, 2 920w, 2 200s, and 1 740vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.3 (2 H, m, ArH), 7.7 (3 H, m, ArH), and 2.8 (3 H, s, SMe); *m/z* 244 (M^+).

Compounds (**7b—f**) were prepared in the same method as described in the preparation of (**7a**).

5-*Cyano*-2-(p-*methoxyphenyl*)-4-*methylthio*-1,3-*oxazin*-6-*one* (**7b**): orange crystals, m.p. 201—203 °C (Found: C, 57.2; H, 3.7; N, 10.1. $C_{13}H_{10}N_2O_3S$ requires C, 56.92; H, 3.67; N, 10.21%); $\nu_{max.}$(KBr) 3 060w, 2 920m, 2 810m, 2 200s, and 1 740 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.25 (2 H, d, *J* 9 Hz, ArH), 7.0 (2 H, d, *J* 9 Hz, ArH), 3.9 (3 H, s, MeO), and 2.8 (3 H, s, SMe); *m/z* 274 (M^+).

2-(p-*Chlorophenyl*)-5-*cyano*-4-*methylthio*-1,3-*oxazin*-6-*one* (**7c**): orange crystals, m.p. 201—203 °C (Found: C, 51.8; H, 2.6; N, 10.0. $C_{12}H_7ClN_2O_2$ requires C, 51.71; H, 2.53; N, 10.05%); $\nu_{max.}$(KBr) 3 050m, 2 900w, 2 210s, and 1 740vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.2 (2 H, d, *J* 9 Hz, ArH), 7.5 (2 H, d, *J* 9 Hz, ArH), and 2.8 (3 H, s, SMe); *m/z* 278 (M^+).

5-*Cyano*-4-*methylthio*-2-(2-*naphthyl*)-1,3-*oxazin*-6-*one* (**7d**): yellow crystals, m.p. 263—264 °C (Found: C, 65.4; H, 3.5; N, 9.4. $C_{16}H_{10}N_2O_2S$ requires C, 65.29; H, 3.42; N, 9.52%); $\nu_{max.}$(KBr) 3 040, 3 000w, 2 900w, 2 210s, and 1 750vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.9—7.6 (7 H, m, naphthyl) and 2.85 (3 H, s, SMe); *m/z* 294 (M^+).

5-*Cyano*-4-*methylthio*-2-(p-*nitrophenyl*)-1,3-*oxazin*-6-*one* (**7e**): orange crystals, m.p. 213—214 °C (Found: C, 49.8; H, 2.5; N, 14.4. $C_{12}H_7N_3O_4S$ requires C, 49.83; H, 2.44; N, 14.53%); $\nu_{max.}$(KBr) 3 080m, 2 800m, 2 210s, and 1 765vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.5 (4 H, m, ArH) and 2.8 (3 H, s, SMe); *m/z* 289 (M^+).

5-*Cyano*-2-(2-*furyl*)-4-*methylthio*-1,3-*oxazin*-6-*one* (**7f**): yellow crystals, m.p. 190—191 °C (Found: C, 51.5; H, 2.7; N, 11.8. $C_{10}H_6N_2O_3S$ requires C, 51.28; H, 2.58; N, 11.96%); $\nu_{max.}$(KBr) 3 090s, 2 200s, and 1 740vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.8 (1 H, d, *J* 1.7 Hz, furyl), 7.6 (1 H, d, *J* 3.6 Hz, furyl), 6.7 (1 H, m, furyl), and 2.76 (3 H, s, SMe); *m/z* 234 (M^+).

Pyridinium Salt of N-*Benzoyl*-2-*cyano*-3-*hydroxy*-3-(*methylthio*)*acrylamide* (**8**).—A mixture of compound (**2**) (474 mg, 3 mmol), chloroform (10 ml), and pyridine (0.7 ml) was stirred for 10 min at room temperature. To the mixture was added benzoyl chloride (1 ml, 9 mmol). The resultant mixture was stirred for 5 min at the same temperature. The white crystals produced were collected and washed with ethanol, to give the *title salt* as white crystals, m.p. 175—176 °C (Found: C, 59.8; H, 4.4; N, 12.25. $C_{17}H_{15}N_3O_3S$ requires C, 59.81; H, 4.43; N, 12.31%); $\nu_{max.}$(KBr) 3 040w, 2 800—2 900m, 2 180s, 1 690vs, and 1 640vs cm^{-1}.

The pyridine salt was treated with dil. HCl to give (quantitatively) pale yellow crystals of N-*benzoyl*-2-*cyano*-3-*hydroxy*-3-(*methylthio*)*acrylamide* (**9**), m.p. 145—146 °C (Found: C, 54.9; H, 3.8; N, 10.7. $C_{12}H_{10}N_2O_3S$ requires C, 54.95; H, 3.84; N, 10.68%); $\nu_{max.}$(KBr) 3 400br, 3 040w, 2 980s, 2 900m, 2 200s, 1 680vs, and 1 640vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 13.5 (1 H, br, NH or OH), 13.2 (1 H, br, OH or NH), 8.1 (2 H, m, ArH), 7.7 (3 H, m, ArH), and 2.5 (3 H, s, SMe).

Conversion of Amide (**9**) *into oxazinone* (**7a**).—To a solution of PPSE prepared from phosphorus pentaoxide (0.5 g), hexamethyldisiloxane (1 ml), and chloroform (5 ml) by the same method as described in the preparation of compound (**7a**) was added the amide (**9**) (136 mg, 0.52 mmol). The mixture was stirred and heated at 120 °C for 3 h and then quenched with water. The crystals obtained were collected and washed with ethanol to give the oxazinone (**7a**) as an orange powder (50 mg, 40%).

Reaction of Oxazinone (**7a**) *with Phenylhydrazine*.—A mixture of compound (**7a**) (68.6 mg, 0.28 mmol), phenylhydrazine (0.027 ml), and dry benzene (2 ml) was stirred and refluxed for 1 h. To the chilled mixture was added dil. HCl. The organic layer was separated and evaporated to give a yellow oil, which was purified in the usual way by t.l.c. with ethyl acetate–hexane (1:1) as eluant to afford 5-cyanomethyl-1,3-diphenyl-1*H*-1,2,4-triazole[6] in 99% yield.

5-*Cyano*-6-*methylthio*-2,3-*diphenylpyrimidin*-4(3H)-*one* (**14a**) *and* 5-*Cyano*-6-*methylthio*-1,2-*diphenylpyrimidin*-4(1H)-*one* (**15a**).—The reaction was performed at 150—160 °C for 3 h under the same conditions as described in the preparation of compound (**7a**), except that the anilino amide (**3a**) was used in place of compound (**2**). The orange crystalline product was separated in the usual way by t.l.c. with ethyl acetate–benzene (1:4) as eluant; compound (**14a**) was obtained as the faster moving product in 49% yield, and its isomer (**15a**) as the slower moving product in 11% yield; *compound* (**14a**): orange crystals (from EtOH), m.p. 236—237 °C (Found: C, 67.8; H, 4.2; N, 13.2. $C_{18}H_{13}N_3OS$ requires C, 67.69; H, 4.10; N, 13.16%); $\nu_{max.}$(KBr) 3 050w, 2 220s, and 1 680vs cm^{-1}; δ_H (60 MHz; $CDCl_3$–CD_3SOCD_3) 8.05 (2 H, m, ArH), 7.65 (3 H, m, ArH), 7.35 (5 H, s, Ph), and 2.7 (3 H, s, SMe); *m/z* 319 (M^+). *Compound* (**15a**): orange crystals (from EtOH), m.p. 244—245 °C (Found: C, 67.8; H, 4.15; N, 13.2%); $\nu_{max.}$(KBr) 3 040w, 2 220s, and 1 645vs cm^{-1}; δ_H (60 MHz; $CDCl_3$–CD_3SOCD_3) 7.35 (7 H, m, ArH), 7.1 (3 H, m, ArH), and 2.75 (3 H, s, SMe); *m/z* 319 (M^+).

Compounds (**14b**), (**15b**), (**14c**), and (**15c**) were prepared by the same method, using the appropriate carboxylic acid.

5-*Cyano*-6-*methylthio*-2-(p-*nitrophenyl*)-3-*phenylpyrimidin*-4(3H)-*one* (**14b**): orange crystals (from EtOH), m.p. 268—269 °C, yield 54% (Found: C, 59.2; H, 3.45; N, 15.1. $C_{18}H_{12}N_4O_3S$ requires C, 59.33: H, 3.32; N, 15.38%); $\nu_{max.}$(KBr) 3 050w, 2 900w, 2 220m, and 1 670s cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.1 (2 H, d, *J* 9 Hz, ArH), 7.5 (2 H, d, *J* 9 Hz, ArH), 7.4 (3 H, m, Ph), 7.1 (2 H, m, Ph), and 2.67 (3 H, s, SMe); *m/z* 364 (M^+).

5-Cyano-6-methylthio-2-(*p*-nitrophenyl)-1-phenylpyrimidin-4(1*H*)-one (**15b**): orange crystals (from EtOH), m.p. 213—214 °C, yield 24%; $\nu_{max.}$(KBr) 3 040m, 2 900, 2 840m, 2 220m, and 1 640s cm^{-1}; *m/z* 364 (M^+).

2-(p-*Chlorophenyl*)-5-*cyano*-6-*methylthio*-3-*phenylpyrimidin*-4(3H)-*one* (**14c**): orange crystals (from EtOH; 47%), m.p. 197—198 °C (Found: C, 61.1; H, 3.4; N, 11.9. $C_{18}H_{12}ClN_3OS$ requires C, 61.09; H, 3.42; N, 11.88%); $\nu_{max.}$(KBr) 3 030w, 2 930w, 2 900w, 2 210s, and 1 670vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.1—7.4 (9 H, m, ArH) and 2.67 (3 H, s, SMe); *m/z* 353 (M^+).

2-(*p*-Chlorophenyl)-5-cyano-6-methylthio-1-phenylpyrimidin-4(1*H*)-one (**15c**): orange crystals (from EtOH; 38%), m.p. 173—174 °C; $\nu_{max.}$(KBr) 3 050w, 2 900w, 2 180s, and 1 680s cm^{-1}; *m/z* 353 (M^+).

3-*Anilino*-2-*cyano*-3-*methylthioacrylonitrile* (**16**).—An equimolar mixture of 2-cyano-3,3-bis(methylthio)acrylonitrile and aniline was refluxed in ethanol. Usual work-up gave the *title compound* as white needles (from EtOH; 89%), m.p. 171—172 °C (Found: C, 61.4; H, 4.3; N, 19.6. $C_{11}H_9N_3S$ requires C, 61.37; H, 4.21; N, 19.52%); $\nu_{max.}$(KBr) 3 280vs, 3 000m, 2 200vs, 2 180vs, and 1 590s cm^{-1}; *m/z* 215 (M^+).

Conversion of Compound (**16**) *into the Pyrimidinone* (**14a**).—Condensation of the dinitrile (**16**) with benzoic acid in the presence of PPSE was carried out in the usual way to give pyrimidinone (**14a**) in 62% yield.

3-*Anilino*-N-*benzoyl*-2-*cyano*-3-(*methylthio*)*acrylamide* (**17**).—A mixture of compound (**3a**) (699 mg, 3 mmol), sodium hydride (60% oil dispersion; 450 mg, 9 mmol), and THF (10 ml) was heated at 60 °C for 1 h. To the chilled mixture was added benzoyl chloride (0.7 ml, 6 mmol). The resultant mixture was stirred at room temperature for 8 h then quenched with water and extracted with benzene. The extract was evaporated under reduced pressure to give yellow crystals. Recrystallization from ethanol gave the *title secondary amide* as yellow crystals (687 mg, 68%), m.p. 205—206 °C (Found: C, 64.0; H, 4.5; N, 12.5. $C_{18}H_{15}N_3O_2S$ requires C, 64.08; H, 4.48; N, 12.45%); $\nu_{max.}$(KBr) 3 400s, 3 050m, 2 180vs, and 1 690vs cm^{-1}; δ_H (60 MHz; $CDCl_3$–CD_3SOCD_3) 13.6 (1 H, br, NHCO), 8.0 (1 H, br, NH), 7.0—7.5 (10 H, m, 2 Ph), and 2.1 (3 H, s, SMe); *m/z* 337 (M^+).

Compound (**17**) was quantitatively converted into the pyrimidinone (**15a**) in the presence of PPSE.

3-*Benzamido*-2-*cyano*-3-*methylthio*-N-*phenylacrylamide* (**18**).—A mixture of compound (**14a**) (45 mg, 0.14 mmol), ethanol (5 ml), and 10% aqueous NaOH (1 ml) was stirred at room temperature for 2 h. The white crystals produced were collected and washed with ethanol to give the *diamide* (**18**) as white crystals (m.p. 207 °C) in nearly quantitative yield (Found: C, 63.9; H, 4.6; N, 12.3. $C_{18}H_{15}N_3O_2S$ requires C, 64.08; H, 4.48; N, 12.45%); $\nu_{max.}$(KBr) 3 280s, 2 200s, and 1 710s cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.1 (2 H, m, ArH), 7.9 (1 H, s, NH), 7.7—7.2 (8 H, m, ArH), 3.9 (1 H, s, NH), and 2.7 (3 H, s, SMe); *m/z* 337 (M^+).

Conversion of diamide (**18**) into the pyrimidinone (**14a**) was performed in the usual way with PPSE (yield 99%).

S-*Methyl Cyano*(*phenyl*)*thioacetate* (**4a**).—A mixture of phenylacetonitrile (1.17 g, 10 mmol), *SS*-dimethyl dithiocarbonate (1.34 g, 11 mmol), sodium hydride (60% oil dispersion; 1 g) (free from oil), and THF (30 ml) was stirred at room temperature for 2 days, and then quenched with water. The aqueous solution was washed with benzene, acidified with dil. HCl, and extracted with benzene. The extract was dried over sodium sulphate and evaporated under reduced pressure to give the title thioester as a yellow oil, which was, in turn, purified on a short column of silica gel with benzene as eluant to give a *yellow oil* (1.2 g, 62%), b.p. 110 °C/0.1 mmHg (Found: C, 62.6; H, 4.8; N, 7.3. $C_{10}H_9NOS$ requires C, 62.80; H, 4.74; N, 7.32%); $\nu_{max.}$(neat) 3 040, 3 020s, 2 900s, 2 250s, and 1 680vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.45 (5 H, s, Ph), 4.80 (1 H, s, CH), and 2.35 (3 H, s, SMe); *m/z* 191 (M^+).

S-*Methyl* 2-*Cyanothiopropionate* (**4b**).—To a mixture of lithium di-isopropylamide (LDA) (20 mmol) in THF (20 ml) prepared in the usual way was added propionitrile (0.55 g, 10 mmol) and *SS*-dimethyl dithiocarbonate (1.34 g, 11 mmol) at −78 °C. The mixture was stirred at the same temperature for 6 h and then at room temperature overnight. The reaction mixture was quenched with water and purification was carried out by the same sequence as above; the *title thioester* was obtained as a yellow oil (0.58 g, 45%), b.p. 30 °C/0.1 mmHg (Found: C, 46.5; H, 5.4; N, 10.8. C_5H_7NOS requires C, 46.49; H, 5.46; N, 10.84%); $\nu_{max.}$(neat) 2 990, 2 920s, 2 225s, and 1 690vs

cm^{-1}; δ_H (60 MHz; $CDCl_3$) 3.92 (1 H, q, *J* 4 Hz, CH), 2.46 (3 H, s, SMe), and 1.61 (3 H, d, *J* 4 Hz, Me); *m/z* 129 (M^+).

4-*Methylthio*-2,5-*diphenyl*-1,3-*oxazin*-6-*one* (**13a**).—To neat PPSE, prepared in the usual way from phosphorus pentaoxide (2 g), hexamethyldisiloxane (4 ml), and benzene (5 ml), was added benzoic acid (134 mg, 1.1 mmol). After the mixture was stirred for several min, dry benzene (2 ml) containing thioester (**4a**) (191 mg, 1 mmol) was added to the mixture and the resultant solution was stirred at 160 °C for 2 h, and then quenched with water and extracted with chloroform. The extract was dried (sodium sulphate) and evaporated under reduced pressure to give a brown material. Recrystallization from ethanol gave the *title compound* as yellow needles (85.6 mg, 29%), m.p. 192—193 °C (Found: C, 69.1; H, 4.5; N, 4.8. $C_{17}H_{13}NO_2S$ requires C, 69.13; H, 4.44; N, 4.74%); $\nu_{max.}$(KBr) 3 050w, 2 920w, and 1 730vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.36 (2 H, m, Ph), 7.58 (8 H, m, Ph), and 2.65 (3 H, s, SMe); *m/z* 295 (M^+).

5-*Methyl*-4-*methylthio*-2-*phenyl*-1,3-*oxazin*-6-*one* (**13b**) was prepared from thioester (**4b**) by the same procedure as described above, and was obtained as prisms (from EtOH), m.p. 111—112 °C (Found: C, 61.8; H, 4.75; N, 6.0. $C_{12}H_{11}NO_2S$ requires C, 61.78; H, 4.75; N, 6.00%); $\nu_{max.}$(KBr) 3 030w, 3 000w, 2 910w, 2 880w, and 1 720vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.18 (2 H, m, Ph), 7.59 (3 H, m, Ph), 2.60 (3 H, s, SMe), and 2.00 (3 H, s, Me); *m/z* 233 (M^+).

Use of Phosphoryl Trichloride and Propylphosphonic Acid Cyclic Anhydride as Condensation Reagents

5-*Carbamoyl*-4-*methylthio*-2-*phenyl*-1,3-*oxazin*-6-*one*.—A mixture of compound (**2**) (0.5 mmol), benzoic acid (0.5 mmol), $POCl_3$ (1 ml), and benzene (2 ml) was refluxed for 3 h. The resultant orange crystals were collected and washed with ethanol to give the *title compound* as yellow needles (43 mg, 33%) m.p. 257—258 °C (decomp.) (from EtOH–AcOH) (Found: C, 54.95; H, 3.85; N, 10.6. $C_{12}H_{10}N_2O_3S$ requires C, 54.95; H, 3.84; N, 10.68%); $\nu_{max.}$(KBr) 3 360s, 3 130s, 1 720vs, 1 670s, 1 590s, and 1 560vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.4 (1 H, br, NH), 8.3 (2 H, m, Ph), 7.55 (3 H, m, Ph), 5.60 (1 H, br, NH), and 2.65 (3 H, s, SMe); *m/z* 262 (M^+). This compound could be converted into the nitrile (**7a**) in quantitative yield by treatment with PPSE (120 °C; 2 h).

When 1-propylphosphonic acid cyclic anhydride was used in the condensation of compound (**2**) (120 °C; 3 h), nitrile (**7a**) was isolated in 48% yield.

3-*Anilino*-3-*methylthio*-2-*phenylacrylonitrile* (**5a**).—A mixture of phenylacetonitrile (1.17 g, 10 mmol), sodium hydride (60% oil dispersion; 1 g) free from oil, and THF (50 ml) was refluxed for 2 h and to the mixture was added phenyl isothiocyanate (1.48 g, 11 mmol) at <0 °C. The resultant mixture was stirred at room temperature for 1 h and then quenched with water. The aqueous layer was washed with benzene and stirred with methyl iodide at room temperature overnight. The reaction mixture was extracted with benzene, and the extract was then dried (sodium sulphate) and evaporated under reduced pressure to give the *title acrylonitrile* (2.5 g, 94%) as yellow crystals recrystallized as pale yellow crystals (from EtOH) (Found: C, 72.1; H, 5.4; N, 10.5. $C_{16}H_{14}N_2S$ requires C, 72.15; H, 5.30; N, 10.52%); $\nu_{max.}$(KBr) 3 220s, 3 000w, and 2 180vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.25 (10 H, m, 2 × Ph), 6.77 (1 H, br, NH), and 2.21 and 1.98 (3 H, s, SMe, *E,Z* mixture); *m/z* 266 (M^+).

3-*Anilino*-2-*methyl*-3-*methylthioacrylonitrile* (**5b**).—The preparation of compound (**5b**) was carried out by the same procedure as mentioned above, but with LDA in place of sodium hydride as base; the *title nitrile* was obtained as yellow prisms (2.0 g, 99%), m.p. 81—83 °C (Found: C, 64.55; H, 5.9; N, 13.7. $C_{11}H_{12}N_2S$ requires C, 64.67; H, 5.92; N, 13.71%); $\nu_{max.}$(neat) 3 250s, 3 000w, 2 900w, 2 830m, and 2 190 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.13 (5 H, m, Ph), 6.55 (1 H, br, NH), 2.45 and 2.20 (3 H, s, SMe), and 2.05 and 1.80 (3 H, s, Me); *m/z* 204 (M^+). N.m.r. data showed compound (**5b**) to be an *E,Z* mixture.

Ethyl 3-*Anilino*-2-*cyano*-3-(*methylthio*)*acrylate* (**5c**).—This compound was prepared by the reaction of aniline with ethyl 3,3-bis(methylthio)-2-cyanoacrylate, which was derived from ethyl cyanoacetate and dimethyl trithiocarbonate; the *title ester* was obtained as yellow plates (1.5 g, 59%) (from EtOH) m.p. 81—82 °C (Found: C, 59.2; H, 5.35; N, 10.6. $C_{13}H_{14}N_2O_2S$ requires C, 59.52; H, 5.38; N, 10.68%); $\nu_{max.}$(KBr) 3 140w, 3 040w, 2 950w, 2 900w, 2 200vs, and 1 660vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 11.5 (1 H, br, NH), 7.28 (5 H, s, Ph), 4.20 (2 H, q, *J* 4 Hz, CH_2), 2.39 (3 H, s, SMe), and 1.39 (3 H, t, *J* 4 Hz, Me); *m/z* 262 (M^+).

6-*Methylthio*-2,3,5-*triphenylpyrimidin*-4(3H)-*one* (**19a**).—To a PPSE solution in benzene prepared from phosphorus pentaoxide (2 g), hexamethyldisiloxane (4 ml), and benzene (5 ml) in the usual way were added benzoic acid (122 mg, 1 mmol) and nitrile (**5a**) (266 mg, 1 mmol). The mixture was refluxed for 2 h, quenched with water, and extracted with benzene. The extract was dried (sodium sulphate) and evaporated under reduced pressure to give brown crystals; recrystallization (EtOH) gave the *title ketone* as white needles (259 mg, 70%), m.p. 236—237 °C (Found: C, 74.55; H, 5.0; N, 7.5. $C_{23}H_{18}N_2OS$ requires C, 74.57; H, 4.90; N, 7.56%); $\nu_{max.}$(KBr) 3 040w, 2 990w, 2 920w, and 1 680vs cm^{-1}; δ_H (60 MHz; $CDCl_3$), 7.30 (15 H, m, 3 × Ph), and 2.50 (3 H, s, SMe); *m/z* 370 (M^+).

5-*Methyl*-6-*methylthio*-2,3-*diphenylpyrimidin*-4(3H)-*one* (**19b**) *and Ethyl* 3,4-*Dihydro*-6-*methylthio*-4-*oxo*-2,3-*diphenylpyrimidine*-5-*carboxylate* (**19c**).—These compounds were prepared by the same method as mentioned above, from the corresponding nitrile (**5b** and **c**). *Ketone* (**19b**): orange needles (from EtOH) (234 mg, 76%), m.p. 116—118 °C (Found: C, 69.9; H, 5.2; N, 9.15. $C_{18}H_{16}N_2OS$ requires C, 70.10; H, 5.23; N, 9.08%); $\nu_{max.}$(KBr) 3 030w, 2 940w, and 1 660vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.85 (2 H, m, Ph), 7.25 (8 H, m, 2 × Ph), 2.60 (3 H, s, SMe), and 2.10 (3 H, s, Me); *m/z* 308 (M^+).

Ester (**19c**): white needles (from EtOH) (256 mg, 70%), m.p. 179—180 °C (Found: C, 65.3; H, 5.1; N, 7.6. $C_{20}H_{18}N_2O_3S$ requires C, 65.56; H, 4.95; N, 7.65%); $\nu_{max.}$(KBr) 3 050w, 2 980w, 2 920w, 2 850w, and 1 700vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.10 (10 H, m, 2 × Ph), 4.28 (2 H, q, *J* 4 Hz, CH_2), 2.56 (3 H, s, SMe), and 1.40 (3 H, t, *J* 4 Hz, Me); *m/z* 366 (M^+).

2-*Cyano*-3-*mercapto*-3-(*methylseleno*)*acrylamide* (**6**).—A mixture of sodium hydride (free from oil) (16 mmol), cyanoacetamide (336 mg, 4 mmol), and THF (20 ml) was refluxed for 1 h. The resulting mixture was cooled to 0 °C and then Se,Se'-dimethyl thiodiselenocarbonate[10] (928 mg, 4 mmol) was added dropwise to the solution. The mixture was stirred for 24 h, quenched with water, washed with benzene, and extracted with ethyl acetate with addition of dil. HCl. The extract was treated with charcoal and then evaporated under reduced pressure to give yellow plates of the selenide (**6**), (550 mg, 62%), m.p. 135—136 °C; $\nu_{max.}$(KBr) 3 380, 3 280, 3 200s, 2 200vs, 1 680, 1 640vs, and 1 540vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 16.65 (1 H, s, SH), 6.25 and 5.75 (2 H, br, NH_2), and 2.55 (3 H, s, SeMe). Compound (**6**) decomposed on attempted recrystallization.

Table 6. Atomic co-ordinates of compound (**14a**). Crystallographic numbering scheme is used

Atom	*x*	*y*	*z*
N(1)	0.611 3(5)	0.434 4(1)	0.712 5(6)
C(2)	0.543 4(2)	0.317 4(5)	0.668 4(4)
N(3)	0.539 1(2)	0.276 9(9)	0.584 7(9)
C(4)	0.608 1(7)	0.350 6(1)	0.541 2(5)
C(5)	0.685 7(6)	0.458 7(0)	0.582 5(4)
C(6)	0.689 8(6)	0.509 1(9)	0.672 1(3)
O(7)	0.750 6(1)	0.611 6(4)	0.712 4(8)
C(8)	0.760 6(1)	0.530 6(9)	0.536 8(6)
N(9)	0.820 1(0)	0.588 4(2)	0.500 2(1)
S(10)	0.598 5(9)	0.306 5(0)	0.428 6(6)
C(11)	0.489 4(0)	0.162 0(9)	0.405 3(2)
C(12)	0.605 2(7)	0.497 0(0)	0.799 8(0)
C(13)	0.690 5(3)	0.470 4(6)	0.869 8(0)
C(14)	0.686 9(0)	0.535 8(6)	0.952 6(7)
C(15)	0.599 1(2)	0.625 9(8)	0.964 7(2)
C(16)	0.514 8(1)	0.650 6(9)	0.894 7(3)
C(17)	0.517 8(5)	0.588 0(1)	0.810 4(9)
C(18)	0.467 9(0)	0.230 7(6)	0.713 6(3)
C(19)	0.497 8(2)	0.169 7(9)	0.799 7(8)
C(20)	0.426 9(5)	0.080 5(6)	0.836 9(4)
C(21)	0.325 3(5)	0.049 0(4)	0.788 5(0)
C(22)	0.296 2(5)	0.106 6(0)	0.702 0(9)
C(23)	0.367 3(4)	0.196 4(4)	0.664 7(2)

5-*Cyano*-4-*methylseleno*-2-*phenyl*-1,3-*thiazin*-6-*one* (**21a**).—To a PPE solution in chloroform [PPE (5 ml) and $CHCl_3$ (7 ml)] were added benzoic acid (200 mg, 1.65 mmol) and selenide (**6**) (364 mg, 1.65 mmol). The mixture was refluxed for 2 h and then most of the solvent was evaporated off to give a deep red oil, which crystallized under ethanol (2—3 ml) in a refrigerator. The resultant brown crystals were collected to give 5-cyano-4-methylseleno-2-phenyl-1,3-oxazine-6-thione (**20a**) (151 mg, 30%). The filtrate was neutralized with aqueous sodium hydrogen carbonate and then extracted with benzene. Evaporation of the extract gave the title thiazinone (**21a**) (184 mg, 36%).

Oxazinethione (**20a**): yellow crystals (Found: C, 47.0; H, 2.8; N, 9.4. $C_{12}H_8N_2OSSe$ requires C, 46.91; H, 2.62; N, 9.12%); $\nu_{max.}$(KBr) 3 040w, 2 900w, 2 200w, 1 590m, 1 550vs, and 1 440vs cm^{-1}; *m/z* 308 (M^+).

Thiazinone (**21a**): yellow crystals (from benzene), m.p. 211—213 °C (Found: C, 46.9; H, 2.6; N, 9.2%); $\nu_{max.}$(KBr) 3 040w, 2 900m, 1 640vs, 1 490vs, and 1 440vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.0 (2 H, m, Ph), 7.6 (3 H, m, Ph), and 2.7 (3 H, s, SeMe); *m/z* 308 (M^+).

Conversion of Compound (**21a**) *into* 5-*Cyanomethyl*-1,3-*diphenyl*-1H-1,2,4-*triazole*.—A mixture of selenide (**21a**) (35 mg, 0.11 mmol), phenylhydrazine (0.06 ml), and dry benzene (1.5 ml) was refluxed for 1.5 h. The reaction mixture was evaporated under reduced pressure to give a red oil, which was purified by t.l.c. with ethyl acetate–hexane (1:2) as eluant in 95% yield. Its i.r. spectrum was superposable on that of an authentic specimen of 5-cyanomethyl-1,3-diphenyl-1H-1,2,4-triazole.

5-*Cyano*-4-*methylseleno*-2-(2-*naphthyl*)-1,3-*thiazin*-6-*one* (**21b**) *and* 5-*Cyano*-2-(p-*methoxyphenyl*)-4-*methylseleno*-1,3-*thiazin*-6-*one* (**21c**).—These compounds were prepared by the same method as described in the preparation of (**21a**), but with the corresponding carboxylic acid. *Thiazinone* (**21b**): yellow crystals (from EtOH) (425 mg, 72%), m.p. 224—225 °C (Found: C, 53.8; H, 2.85; N, 7.9. $C_{16}H_{10}N_2OSSe$ requires C, 53.79; H, 2.82; N, 7.84%); $\nu_{max.}$(KBr) 3 060w, 2 950w, 2 220m, 1 650vs, 1 510vs, and 1 460vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.9 (1 H, s, ArH), 7.9—8.3 (4 H, m, ArH), 7.5—7.8 (2 H, m, ArH), and 2.8 (3 H, s, Me); *m/z* 358 (M^+).

Thiazinone (**21c**): orange powder (from EtOH) (296 mg, 53%), m.p. 208—209 °C (Found: C, 46.6; H, 3.3; N, 8.4. $C_{13}H_{10}N_2O_2SSe$ requires C, 46.30; H, 2.99; N, 8.31%); $\nu_{max.}$(KBr) 3 060w, 2 930m, 2 200m, 1 640vs, 1 600s, and 1 490vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.0 (2 H, dd, ArH), 7.3 (2 H, dd, ArH), 3.9 (3 H, s, OMe), and 2.7 (3 H, s, SeMe); *m/z* 338 (M^+).

5-*Cyano*-6-*methylseleno*-2-*phenyl*-1,3-*thiazin*-4-*one* (**22**).—To a mixture of compound (**6**) (485 mg, 2.1 mmol), pyridine (0.5 ml), and chloroform (4 ml) was added benzoyl chloride (0.7 ml). The resulting mixture was refluxed for 2 h and then evaporated under reduced pressure to give a red oil, to which ethanol and water were added to give a brown precipitate (371 mg, 58%). Recrystallization from ethanol gave brown crystals of the *title thiazinone*, m.p. 173—174 °C (decomp.) (Found: C, 47.2; H, 2.7; N, 9.2. $C_{12}H_8N_2OSSe$ requires C, 46.91; H, 2.62; N, 9.12%); $\nu_{max.}$(KBr) 3 040w, 2 900w, 2 200s, 1 650vs, and 1 550vs cm^{-1}; δ_H (60 MHz; $CDCl_3$) 8.1 (2 H, m, Ph), 7.6 (3 H, m, Ph), and 2.7 (3 H, s, SeMe); *m/z* 308 (M^+).

X-*Ray Crystal Structure Determination of Compound* (**14a**).—Crystals were prepared by slow evaporation of an ethanolic solution.

Crystal data. $C_{18}H_{13}N_3OS$, M = 319.37, monoclinic, a = 12.861(5), b = 8.093(2), c = 15.352(5) Å, β = 101.82(3)°, V = 1 564.0 $Å^3$, space group $P2_1/n$, Z = 4, D_x = 1.356 g cm^{-1}.

Data collection and processing. An AFC5 diffractometer was used, in ω/2θ mode with scan speed 4.0° min^{-1}; graphite-monochromated Cu-K_α radiation was used; 3 719 reflections were measured (2θ range $3° \leq 2\theta \leq 155°$, $+h$, $+k$, $\pm l$) 2 280 were given a unique absorption correction (average transmission factor 0.14), giving 2 016 reflections with $I > 2\sigma(I)$.

Structure analysis and refinement. The structure was solved by the UNICS-III system (Library of Computer Center of Tokyo University) based on direct methods, and refined to a final R value of 0.058 (R_w 0.064, blocked full-matrix least-squares refinement). Hydrogen atoms were located by the difference Fourier method using practical reflection data. Atomic co-ordinates are listed in Table 6. Bond lengths and angles and thermal parameters are available as a Supplementary publication SUP No. 56536 (4 pp.)].*

* For details of the Supplementary publications scheme, see Instructions for Authors (1986), *J. Chem. Soc., Perkin Trans. 1*, 1986, Issue 1.

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