4-*H*, 1), 7.13-7.60 (m, aromatic *H*, 15), and 8.15-8.40 (br s, pyrrole N-*H*, 1); exact mass calcd for $C_{23}H_{19}N$, 309.1517; found, 309.1523.

Anal. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.41; H, 6.05; N, 4.41.

Acknowledgment. We acknowledge support of this research by the National Cancer Institute (5-R01-CA11185) and the Stauffer Chemical Co.

Registry No. **1**, 68058-80-0; **4**, 75096-67-2; **5**, 13219-95-9; **6**, 86863-97-0; **7**, 838-40-4; **12**, 86863-98-1; **13**, 1889-67-4; **15**, 86863-99-2; **20**, 86864-00-8; **21**, 86864-01-9; **25**, 86864-02-0; **26**, 86864-03-1; **29**, 86864-04-2; **31a**, 100-66-3; **31b**, 108-88-3; **35**, 70487-20-6; **38a**, 70487-19-3; **38b**, 70487-21-7; **39**, 70487-23-9; **40**, 103-29-7; **42a**, 71-43-2; **42b**, 100-47-0; **42c**, 98-95-3; **46a**, 70487-12-6; **46b** (4-CN), 70487-13-7; **46b'** (5-CN), 70487-14-8; **46b''** (6-CN), 70487-15-9; **46c** (4-NO_2), 70487-16-0; **46c'** (5-NO_2), 70487-17-1; **46c''** (6-NO_2), 70487-18-2; **47a**, 3274-61-1; **47b**, 86864-05-3; **47c**, 70487-22-8; **47d**, 86864-06-4; **47e**, 86864-07-5; **59a**, 62-53-3; **59b**, 100-61-8; **61a**, 86864-08-6; **61b**, 86864-09-7; **62a**, 100-51-6; **62b**, 67-63-0; **62c**, 67-56-1; **64b**, 67-64-1; **65b**, 86864-10-0; **65c**, 86864-11-1; **65d**, 86864-12-2; **72a**, 86864-13-3; **72c**, 86864-14-4; **72d**, 86884-71-1; **72f**, 86864-15-5; **73a**, 86864-16-6; **73b**, 68614-52-8; **73c**, 86864-17-7; **73d**, 86864-18-8; **73e**, 86864-19-9; **73f**, 86864-20-2; **74a**, 70487-21-7; **74d**, 86864-21-3; **74f**, 86864-22-4; **75**, 13220-01-4; cyclohexane, 110-82-7; cumene, 98-82-8; cyclohexene, 110-83-8; allylbenzene, 300-57-2; 2,3-dimethyl-2-butene, 563-79-1; methyl *m*-nitrobenzoate, 618-95-1; thioxanthen-9-one, 492-22-8; 4,4'-bis(dimethylamino)benzophenone, 90-94-8; acetic acid, 64-19-7; benzaldehyde diphenyl thioacetal, 7695-69-4; (*p*-methylbenzylidene)acetophenone, 4224-87-7; benzoin, 119-53-9; (*p*-methyoxybenzylidene)acetophenone, 959-33-1; (*m*-cyanobenzalidine)acetophenone, 62584-53-6; *m*-cyanobenzaldehyde, 24964-64-5; acetophenone, 98-86-2; (*o*-methoxybenzylidene)-acetophenone, 5416-70-6; (*p*-nitrobenzylidene)acetophenone, 1222-98-6; *N,N*-dimethylaniline, 121-69-7.

S,N Double Rearrangement. 3. Reaction Mechanism

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The mechanism of the "S,N double rearrangement" was studied by ^{13}C labeling and crossover reactions. The results indicate that the condensation is a thiallylic rearrangement of the initial ring-closure product formed from the cyano and mercapto groups of the starting compound and benzoic acid.

In a study of the synthesis of 1,3-thiazin-4-ones from 2-cyano-3-mercapto-3-(methylthio)acrylamide (**1a**), we found that **1a** condensed with benzoic acid in the presence of polyphosphate ester (PPE) to give 5-cyano-4-(methylthio)-2-phenyl-1,3-thiazin-6-one (**3a**) via **2a** (Scheme I). We have termed this novel condensation reaction involving interchange of sulfur and nitrogen atoms an "S,N double rearrangement".[1,2]

In a previous paper,[2] we proposed a reaction pathway via a thiete intermediate for this condensation. However, the following three observations cannot be explained by this postulated mechanism (see Scheme II).

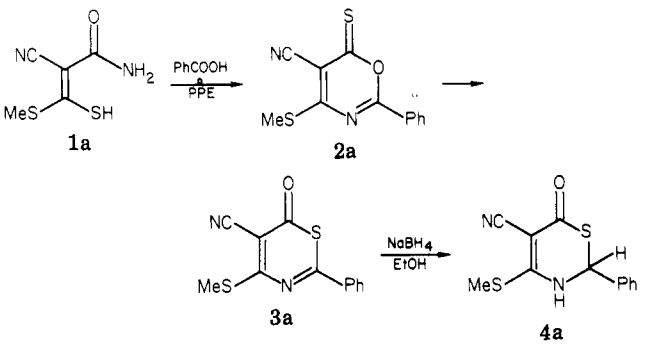
(1) A mixture of **1a** (2.9 mmol), benzoic acid (2.9 mmol), PPE (2 g), and chloroform (12 mL) was refluxed for 60 min to produce **2a**, whereas **5a** was obtained as a main product by employing half that quantity of PPE (eq 1).

(2) The *N*-methyl (**1b**), *N*-ethyl (**1c**), and *N*-benzyl (**1d**) derivatives of **1a** reacted with benzoic acid (2.9 mmol) in the presence of PPE (2 g) to afford the corresponding **5b-d** in 20%, 46%, and 15% yields, respectively (eq 2).

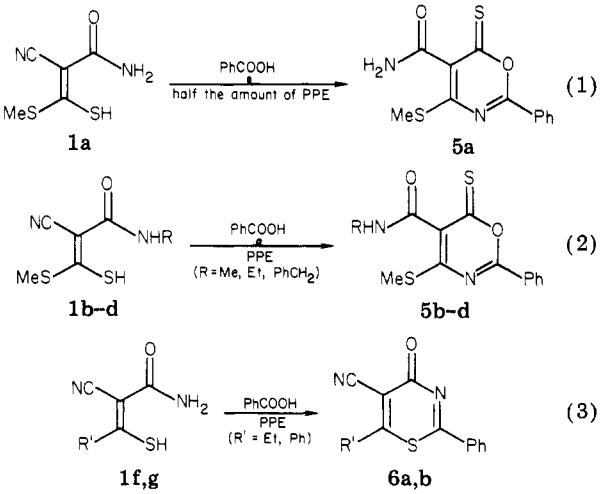
(3) Compounds **1f** and **1g**, having an ethyl or phenyl group, respectively, in place of the SMe group in **1a**, reacted with benzoic acid in the same way to afford unrearranged products, 6-substituted 5-cyano-2-phenyl-1,3-thiazin-4-ones (**6a,b**) in moderate yields (eq 3).

The results of eq 1 and 2 suggest that **5a-d** may be formed by a ring closure involving benzoic acid and the cyano and mercapto groups of **1a**. In this paper we present an alternative to our previous mechanism[2] for the reaction.

Scheme I



Scheme II



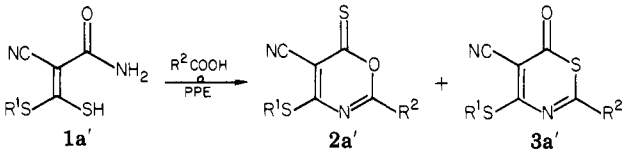
Results and Discussion

First, ^{13}C labeling of the cyano group of **1a** was carried out to elucidate mechanistic features. Compound **2a*** was synthesized from **1a*** and benzoic acid. On being refluxed in ethanol, **2a*** was converted to **3a***,[3] which was reduced

(1) S,N Double Rearrangement. 1: Yokoyama, M.; Nakamura, M.; Imamoto, T.; Yamaguchi, K. *J. Chem. Soc. Chem. Commun.* **1981**, 560.
(2) S,N Double Rearrangement. 2: Yokoyama, M.; Nakamura, M.; Ohteki, H.; Imamoto, T.; Yamaguchi, K. *J. Org. Chem.* **1982**, 47, 1090.

0022-3263/84/1949-0074$01.50/0

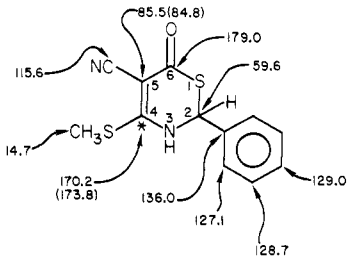
Table I. Preparation of 2a′ and 3a′



1a′ 2a′ 3a′

entry	R^1	R^2	yields, % 2a′	3a′	total
1	Me	β-naphthyl	32	52	84
2	Me	*p*-anisyl	24	69	93
3	Me	*p*-chlorophenyl		59	59
4	Me	*o*-iodophenyl	14	37	51
5	Me	*p*-nitrophenyl		33	33
6	Et	*p*-anisyl	35	27	62
7	Et	*p*-nitrophenyl		31	31
8	CH_2Ph	β-naphthyl		82	82
9	CH_2Ph	*p*-anisyl	62		62
10	CH_2Ph	phenyl		67	67
11	CH_2Ph	*p*-nitrophenyl		27	27
12	Ph	phenyl	23		23

to **4a*** with $NaBH_4$–EtOH.[2] The IR stretching bands of the cyano groups in **2a***, **3a***, and **4a*** were observed at the same frequency as those of **2a**, **3a**, and **4a**, respectively, while the stretching vibrations of their ring-closed structures showed an isotope effect.[4] This result reveals that the cyano groups of **2a***, **3a***, and **4a*** are not enriched with ^{13}C. Further, the methyl, C-6, and C-2 carbon atoms of **3a*** were shown not to be enriched with ^{13}C by comparison of the mass spectrum of **3a** with that of **3a***. The mass spectrum of **3a*** showed characteristic fragment ions at *m/e* 261 (M*), 246 (M* – CH_3), 233 (M* – CO), 200 (M* – COS – H), 154 (M* – COS – SCH_3), and 121 (PhC=S). The mass spectrum of **4a*** confirmed the lack of ^{13}C enrichment of these carbon atoms: *m/e* 263 (M*), 248 (M* – CH_3), 203 (M* – COS), 156 (M* – SCH_3 – COS), and 121 (PhC=S). On the other hand, the ^{13}C NMR spectrum of **4a***[5] revealed that C-4 of **4a*** was enriched with ^{13}C; a very



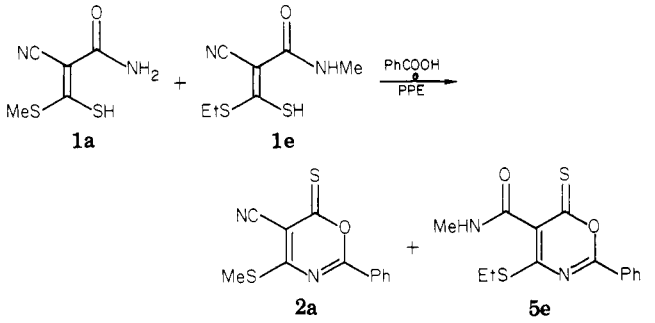
^{13}C NMR (Me_2SO-d_6) data (δ) of **4a***

strong peak appeared at δ 170.2, and a vicinal coupling between ^{13}C-4 and ^{13}C-5 was observed with J = 74 Hz.[6] The numbers in parentheses on the structure show approximate δ values estimated from the chemical shift values of methyl 3-amino-2-cyano-3-(methylthio)acrylate by using incremental values of substituents.[7]

Several compounds of type **1a** were reacted with substituted benzoic acids, with the results summarized in Table I. When **1a** reacted with a benzoic acid containing an electron-donating group, the apparent rate of reaction[8] increased, and the yield was high. Monitoring of the reaction of **1a** with β-naphthoic acid[9] by measuring IR spectra every 5 min revealed that an increase in reaction product was observed with decreasing starting material; no absorptions of intermediates were observed. These results suggest that the rate-determining step of this reaction is the benzoylation of the cyano group of 1a by a "benzoyl-cation-like species"[10] (see Scheme V).

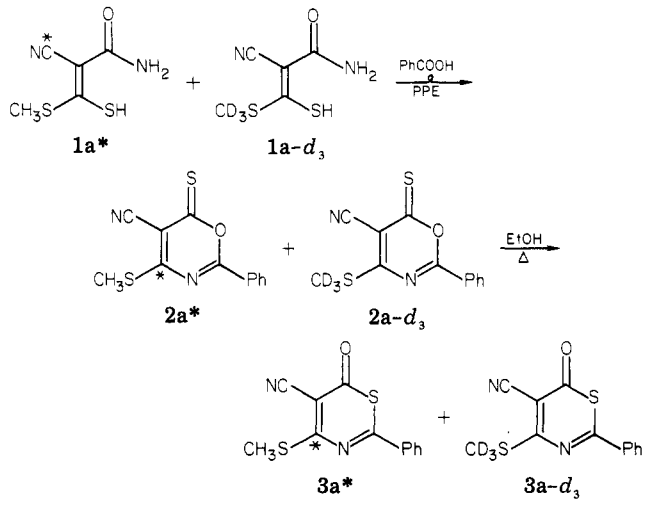
We also carried out two crossover experiments. First, an equimolar mixture of **1a** and **1e** was condensed with benzoic acid to give **2a** and **5e** in 60% and 30% yields,[11] respectively (Scheme III). No crossed compounds were detected. Second, **1a*** and **1a**-d_3[12] were allowed to react in the same way, giving a mixture of **3a*** and **3a**-d_3 in 60%

Scheme III



1a 1e 2a 5e

Scheme IV



1a* 1a-d_3 2a* 2a-d_3 3a* 3a-d_3

(3) The ring transformation was observed on treatment with polar solvents such as alcohols, amines, and dimethyl sulfoxide.

(4) The IR absorptions of **2a** (1440 and 1240 cm^{-1}), **3a** (1445 cm^{-1}), and **4a** (1510 cm^{-1}), **3a*** (1420 cm^{-1}), and **4a*** (1495 cm^{-1}), respectively.

(5) Compound **3a*** decomposed on dissolving in hot Me_2SO. Its ^{13}C NMR measurement proved to be very difficult because of solubility problems. Therefore, **4a*** was adopted for the measurement instead of **3a***.

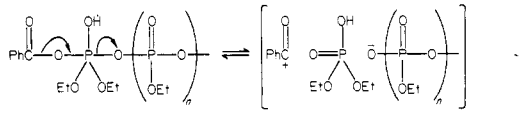
(6) A J_{C-C} value for ethylene is reported to be 67.6 Hz: Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 287.

(7) Silverstein, R. M.; Bassler, G. C.; Morill, T. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1981; p 264.

(8) The rates of disappearance of **1a** were measured: 120 min for *p*-nitrobenzoic acid; 50 min for benzoic acid; 20 min for *p*-methoxybenzoic acid.

(9) The reaction was carried out in chloroform with **1a** (2.9 mmol) and β-naphthoic acid (2.9 mmol) by employing 1 g of PPE and resulted in the formation of 5-carbamoyl-4-(methylthio)-2(β-naphthyl)-1,3-oxazine-6-thione (**5f**). The IR stretching and bending vibrations of the amino groups of **1a** and **5f** were monitored: **1a**, ν(NH_2) 3490 and 3380 cm^{-1}, δ(NH_2) 1538 cm^{-1}; **5f** ν(NH_2) 3520 and 3450 cm^{-1}, δ(NH_2) 1560 cm^{-1}.

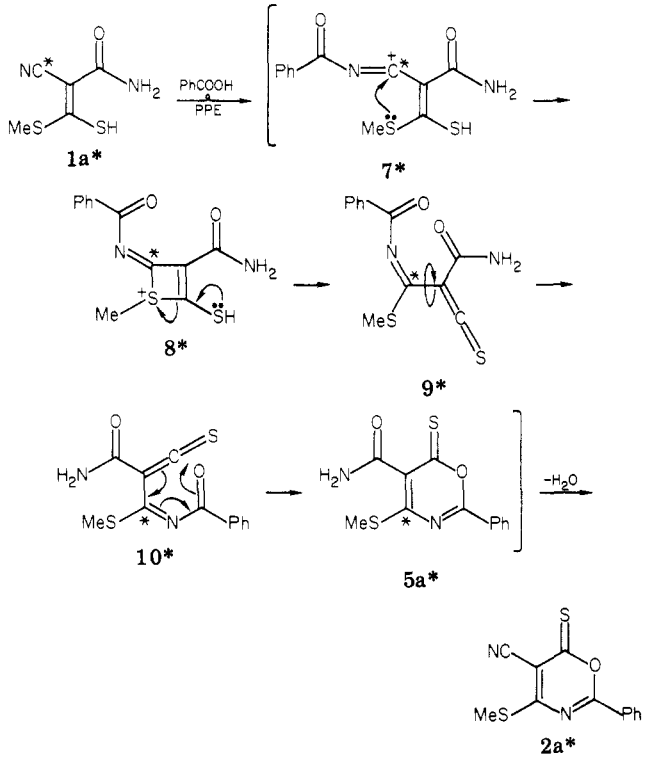
(10) We consider the following species in this reaction:



(11) The yields were calculated on the basis of both **1a** and **1e**.

(12) Compound **1a**-d_3 was prepared by monomethylation of 3,3-bis(ammoniothio)-2-cyanoacrylamide (see ref 2) with CD_3I: white needles ($EtOH$–H_2O); mp 153–154 °C; yield 50%.

Scheme V[a]



[a] C* shows a carbon enriched with ^{13}C.

overall yield[13] (Scheme IV). Although these compounds were not separated, mass spectroscopic analysis[14] of the reaction product showed no crossed compounds. Thus the rearrangement appears to be an intramolecular process.

In conclusion, the rearrangement mechanism shown in Scheme V is proposed on the basis of these experiments. Benzoic acid is initially activated by PPE to generate the "benzoyl-cation-like species".[10] This species is then attacked by the nitrogen of the cyano group in **1a*** to form an active species, **7***, which is spontaneously converted to a sulfonium ion intermediate, **8***, by electron donation from the sulfur atom. Then, **8*** undergoes a facile ring opening due to electron donation by the mercapto group, followed by C–C bond rotation to give **10***, which is, in turn, converted to **5a*** by forming a 1,3-oxazine ring. The presence of a large excess of PPE causes dehydration of **5a*** to afford **2a***.

The intramolecular benzoylation of a cyano group leading to isoquinoline derivatives has been established.[15] Further, as an example of intermolecular acylation of a cyano group, nitriles react with malonyl chloride derivatives to give 1,3-oxazine-4-ones.[16] A thiaallylic rearrangement similar to the process of **7*** → **9*** has been explained by an ion-pair intermediate mechanism.[17] However, in our reaction the more stable sulfonium ion intermediate **8*** is thought to be formed via the analogous allyl cation intermediate **7***. An intermediate similar to **10*** also has been postulated for the formation of 1,3-oxazin-6-ones.[18]

The mechanism of Scheme V can account for the formation of **5a–d** and **6a,b** (eq 1–3). In the reaction of eq 3, owing to the difficulty of formation of **8***, benzoylation of the mercapto groups of **1f,g** gives the unrearranged products **6a,b** (see Scheme II). Consequently, a characteristic feature of this mechanism is the benzoylation of a cyano group, which seems to be a reasonable process in a reaction involving PPE. The use of this rearrangement for the synthesis of heterocycles is presently under investigation.

Experimental Section

General Methods. Microanalyses were performed with a Perkin-Elmer 240 elemental analyser at the Analytical Center of Chiba University. IR, UV, mass, ^1H 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 Laboratory Co. C-60HL and FX-270 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. The reagent PPE was prepared according to the literature.[19]

2-Cyano-3-mercapto-3-(methylthio)acrylamide (1a). Compound **1a**[2] was prepared by the following modified method. To a mixture of sodium hydride (240 mg, 10 mmol) and dry THF (20 mL) was added cyanoacetamide (168 mg, 2 mmol) with stirring at room temperature. The mixture was stirred for 2 h, and there was then added methyl trithiocarbonate (276 mg, 2 mmol). The resulting mixture was further stirred overnight at room temperature, quenched with water, acidified with dilute HCl, and extracted with benzene. The benzene extract was rotary evaporated to give light yellow crystals. Recrystallization from ethanol–water gave **1a** in 65% yield. Compounds **1b,c,e–g**, and **1a**-d_3 were prepared in the same manner. Compound **1d** was prepared by our method.[20] All compounds **1** had the following: IR (KBr) 3250–3330 (NH), 2220–2210 (CN), 1640–1660 (CO) cm^{-1}.

2-Cyano-3-mercapto-3-(methylthio)-*N*-methylacrylamide (1b): from *N*-methylcyanoacetamide and methyl trithiocarbonate; yield 84%; light yellow plates (EtOH); mp 173 °C dec; NMR ($CDCl_3$) δ ca. 16 (br, 1 SH), 6.95 (br, 1, NH), 3.05 (d, 3, NHCH_3), 2.65 (s, 3, SCH_3). Anal. Calcd for $C_6H_8N_2OS_2$: C, 38.28; H, 4.25; N, 14.88; S, 34.06. Found: C, 38.16; H, 4.32; N, 14.91; S, 34.31.

2-Cyano-3-mercapto-3-(methylthio)-*N*-ethylacrylamide (1c): from *N*-ethylcyanoacetamide and methyl trithiocarbonate; yield 75%; white needles (EtOH); mp 161–162 °C; NMR ($CDCl_3$) δ ca. 16 (br, 1, SH), 7.0(br, 1, NH), 3.55 (q, 1, CH_2, J = 7 Hz), 2.65 (s, 3, SCH_3), 1.30 (t, 3, CH_2CH_3, J = Hz). Anal. Calcd for $C_7H_{10}N_2OS_2$: C, 41.57; H, 4.98; N, 13.84; S, 31.70. Found: C, 41.55; H, 4.99; N, 13.79; S, 32.00.

2-Cyano-3-(ethylthio)-3-mercapto-*N*-methylacrylamide (1e): from *N*-methylcyanoacetamide and ethyl trithiocarbonate; yield 80%; light yellow needles (EtOH); mp 144–145 °C. Anal. Calcd for $C_7H_{10}N_2OS_2$: C, 41.56; H, 4.98; N, 13.85; S, 31.70. Found: C, 41.53; H, 4.90; N, 13.81; S, 31.50.

2-Cyano-3-ethyl-3-mercaptoacrylamide (1f): from cyanoacetamide and methyl dithiopropionate; yield 70%; white needles (hexane–benzene); mp 81–82 °C; NMR ($CDCl_3$) δ 10.2 (br, 1, SH),

(13) A mixture of **3a*** and **3a**-d_3: yellow needles; mp 207–208 °C. Compounds **2a**-d_3 and **3a**-d_3 were synthesized independently in the usual way. **2a**-d_3: reddish orange needles ($CHCl_3$–CCl_4–Et_2O); mp 194–195 °C dec; yield 60%. **3a**-d_3: yellow needles; mp 207–208 °C.

(14) The mass data were measured at 30 positions under the stabilized ion intensity. Mass spectrum of reaction products (a mixture of **3a*** and **3a**-d_3), m/e (relative intensity 260 (12.13 ± 2.12), 261 (100), 262 (20.30 ± 3.04), 263 (115.41 ± 5.69), 264 (21.47 ± 3.22), 265 (13.12 ± 2.38); mass spectrum of **3a***, m/e (relative 260 (11.48 ± 1.02), 261 (100), 262 (17.70 ± 2.19), 263 (11.46 ± 1.31); mass spectrum of **3a**-d_3, m/e (relative intensity) 263 (100), 264 (16.98 ± 0.55), 265 (10.98 ± 0.55). The agreement between the relative intensity of m/e 260 of the reaction products and one peak for **3a*** is within the standard deviation. Therefore, the reaction products contained no crossed compounds.

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6.5(br, 2, NH_2), 2.85(q, 2, CH_2, J = 7 Hz), 1.35 (t, 3, CH_3, J = 7 Hz). Anal. Calcd for $C_6H_8N_2OS$: C, 46.14, H, 5.16; N, 17.93; S, 20.53. Found: C, 46.12; H, 5.08; N, 17.89; S, 20.64.

2-Cyano-3-mercapto-3-phenylacrylamide (1g): from cyanoacetamide and methyl dithiobenzoate; yield 80%; light yellow needles (hexane–benzene); mp 143–144 °C. Anal. Calcd for $C_{10}H_8N_2OS$: C, 58.81; H, 3.95; N, 13.72; S, 15.70. Found: C, 58.78; H, 3.95; N, 13.75; S, 15.93.

Compound 1a* (^{13}C-labeled cyano group of 1a) was obtained from methyl trithiocarbonate and $N^{13}CCH_2CONH_2$, which was synthesized from chloroacetic acid and 90% ^{13}C-enriched KCN.[21] In the IR spectrum of **1a***, two stretching bands were observed at 2200 (CN) and 2150 cm^{-1} (^{13}CN) in a ratio of 1:9.

4-Mercapto-5-[(methylamino)carbonyl]-2-phenyl-1,3-oxazine-6-thione (5b). A mixture of **1b** (545 mg, 2.9 mmol), benzoic acid (0.35 g, 2.9 mmol), PPE (2 g), and chloroform (12 mL) was refluxed for 30 min. The reaction mixture was rotary evaporated to give an orange product. Recrystallization from $CHCl_3$–ether gave reddish orange needles: yield 20%; mp 182–183 °C; IR (KBr) 3200 (NH), 1650 (CO) cm^{-1}; NMR(Me_2SO-d_6) δ 8.55 (br, 1, NH), 8.25 (m, 2, Ph), 7.65 (m, 3, Ph); mass spectrum, m/e 292 (M^+), 277 (M – CH_3), 245 (M – SCH_3), 174 (M – COS – CH_3NHCO). Anal. Calcd for $C_{13}H_{12}N_2O_2S_2$: C, 53.40; H, 4.10; N, 9.58; S, 21.98. Found: C, 53.44; H, 4.21; N, 9.73; S, 21.77. In the similar way, compounds **5c–e** and **6a,b** were prepared.

5-[(Ethylamino)carbonyl]-4-(methylthio)-2-phenyl-1,3-oxazine-6-thione (5c): from **1c**; yield 46%; yellow-orange needles (CCl_4); mp 196–197 °C; IR (KBr) 3200 (NH), 3030 (arom CH), 2860–2960 (CH), 1640 (CO) cm^{-1}; NMR ($CDCl_3$) δ 9.45 (br, 1, NH), 8.20 (m, 2, Ph), 7.50(m, 3, Ph), 3.55 (q, 1, CH_2, J = 7 Hz), 3.40 (q, 1, CH_2, J. = 7 Hz), 2.55 (s, 3, SCH_3), 1.30 (t, 3, CH_3, J = 7 Hz); mass spectrum , m/e 306 (M^+), 291 M – CH_3), 259 (M – SCH_3), 105 (PhCO). Anal. Calcd for $C_{14}H_{14}N_2O_2S_2$: C, 54.88; H, 4.61; N, 9.14; S, 20.93. Found: C, 54.86; H, 4.55; N, 9.18; S, 21.13.

5-[(Benzylamino)carbonyl]-4-(methylthio)-2-phenyl-1,3-oxazine-6-thione (5d): from **1d**; yield 15%; yellowish needles (AcOH); mp 156–157 °C; IR (KBr) 3190 (NH), 3010 (arom CH), 2900 (CH), 1640 (CO) cm^{-1}; mass spectrum, m/e 368 (M^+), 353 (M – 15), 321 (M – SCH_3), 105 (PhCO). Anal. Calcd for $C_{19}H_{16}N_2O_2S_2$: C, 61.93; H, 4.38; N, 7.60; S, 17.40. Found: C, 61.88; H, 4.36; N, 7.63; S, 17.20.

4-Ethyl-5-[(methylamino)carbonyl]-2-phenyl-1,3-oxazine-6-thione (5e); reddish orange plates (CCl_4); mp 181–182 °C; IR (KBr) 3220 (NH), 3050 (arom CH), 2850–2950 (CH), 1640 (CO) cm^{-1}; mass spectrum, m/e 306 (M^+), 277 (M – C_2H_5), 245 (M – SC_2H_5), 105 (PhCO). Anal. Calcd for $C_{14}H_{14}N_2O_2S_2$: C, 54.88; H, 4.61; N, 9.14; S, 20.93. Found: C, 54.76; H, 4.63; H, 4.63; N, 9.22; S, 21.20.

5-Cyano-6-ethyl-2-phenyl-1,3-thiazin-4-one (6a): yield 50%; light brown crystals (EtOH); mp 116–117 °C; IR (KBr) 3020 (arom CH), 2950 (CH), 2220 (CN), 1660 (CO) cm^{-1}; NMR ($CDCl_3$) δ 7.85 (m, 2, Ph), 7.30 (m, 3, Ph), 2.60 (q, 2, CH_2, J = 7 Hz), 1.35 (t, 3, CH_3, J = 7 Hz); mass spectrum, m/e 242 (M^+), 111 (M – PhC=NCO). Anal. Calcd for $C_{13}H_{10}N_2OS$: C, 64.44; H, 4.16; N, 11.65; S, 13.23. Found: C, 64.56; H, 4.18; N, 11.53; S, 13.33.

5-Cyano-2,6-diphenyl-1,3-thiazin-4-one (6b): yield 58%; white crystals (EtOH); mp 218–219 °C; IR (KBr) 3030 (arom CH), 2210 (CN), 1660 (CO) cm^{-1}; mass spectrum, m/e 290 (M^+), 159 (M – PhC=NCO). Anal. Calcd for $C_{17}H_{10}N_2OS$: C, 70.33; H, 3.47; N, 9.65; S, 11.04. Found: C, 70.28; H, 3.47; N, 9.66; S, 10.95.

Compounds **2a′** and **3a′** were prepared from substituted benzoic acids (2.9 mmol), **1a′** (2.9 mmol), and PPE (2 g). After the reaction was completed, the mixture was rotary evaporated to give a red oil, which was, in turn, treated with ethanol to afford 2a′ as crystals. The filtrate was then stirred overnight with aqueous $NaHCO_3$ solution to give **3a′** as a precipitate. In the case of carboxylic acids with electron-withdrawing groups (entries 3, 5, 7, and 11), compounds **3a′** were formed exclusively, owing to a facile ring transformation on treatment with ethanol.

5-Cyano-4-(methylthio)-2-(β-naphthyl)-1,3-oxazine-6-thione (entry 1, 2a′): Orange crystals ($CHCl_3$); mp 237–238 °C; IR (KBr) 2220 (CN) cm^{-1}; mass spectrum, m/e 310 (M^+), 249 (M – COS – HO). Anal. Calcd for $C_{16}H_{10}N_2OS_2$: C, 61.91; H, 3.25; N, 9.02; S, 20.66. Found: C, 61.96; H, 3.23; N, 8.99; S, 20.58.

5-Cyano-4-(methylthio)-2-(β-naphthyl)-1,3-thiazin-6-one (entry 1, 3a′): brown crystals (pyridine–H_2O); mp 217–218 °C; IR (KBr) 2220 (CN), 1650 (CO) cm^{-1}; mass spectrum, m/e 310 (M^+), 249 (M –COS – H).

2-(p-Anisyl)-5-cyano-4-(methylthio)-1,3-oxazine-6-thione (entry 2, 2a′): yellow needles (AcOH); mp 201–202 °C; IR (KBr) 2830–2950 (CH), 2210 (CN); NMR (Me_2SO-d_6) δ 8.25 (d, 2, Ph, J = 6 Hz), 8.0 (d, 2, Ph, J = 6 Hz), 3.85 (s, 3, OCH_3), 2.70 (s, 3, SCH_3); mass spectrum, m/e 290 (M^+), 229 (M – COS – H), 275 (M – CH_3), 151 ($CH_3OC_6H_4CS$). Anal. Calcd for $C_{13}H_{10}N_2O_2S_2$: C, 53.77; H, 3.47; N, 9.65; S, 22.09. Found: C, 53.68; H, 345; N, 9.66; S, 22.10.

2-(p-Anisyl)-5-cyano-4-(methylthio)-1,3-thiazin-6-one (entry 2, 3a): yellow crystals (AcOH); 230–231 °C; IR (KBr) 2210 (CN), 1640 (CO) cm^{-1}; mass spectrum, m/e 290 (M^+), 229 (M – COS – H).

2-(p-Chlorophenyl)-5-cyano-4-(methythio)-1,3-thiazin-6-one (entry 3, 3a′): yellow crystals (pyridine–EtOH); mp 224–51 °C IR (KBr) 2200 (CN), 1640 (CO) cm^{-1}; mass spectrum, m/e 294 (M^+), 233 (M – COS – H). Anal. Calcd for $C_{12}H_7N_2OS_2Cl$: C, 48.89; H, 2.39; N, 9.50; S, 21.75. Found: C, 48.90; H, 2.38; N, 9.53; S, 22.00.

5-Cyano-2-(o-iodophenyl)-4-(methylthio)-1,3-oxazine-6-thione (entry 4, 2a′): Orange crystals ($CHCl_3$); mp 188–190 °C; IR (KBr) 2220 (CN); mass spectrum, m/e 385 (M^+), 371 (M – CH_3), 324 (M – COS). Anal. Calcd for $C_{12}H_7N_2OS_2I$: C, 37.32; H, 1.83; N, 7.25; S, 16.60. Found: C, 37.34; H, 1.84; N, 7.28; S, 16.43.

5-Cyano-2-(o-iodophenyl)-4-(methylthio)-1,3-thiazin-6-one (entry 4, 3a′): brown cyrstals (EtOH); mp 181–182 °C; IR (KBr) 2210 (CN), 1635 (CO) cm^{-1}; mass spectrum, m/e 385 (M^+), 324 (M – COS – H).

5-Cyano-4-(methylthio)-2-(p-nitrophenyl)-1,3-thiazin-6-one (entry 5, 3a′): orange prisms (EtOH); mp 226–227 °C; IR (KBr) 3100 (arom CH), 2850–2970 (CH), 1710 (CO) cm^{-1}; mass spectrum, m/e 305 (M^+), 244 (M – COS – H). Anal. Calcd for $C_{12}H_7N_3O_3S_2$: C, 47.20; H, 2.31; N, 13.76; S, 21.00. Found: C, 47.16; H, 2.30; N, 13.79; S, 21.20.

2-(p-Anisyl)-5-cyano-4-(ethylthio)-1,3-oxazine-6-thione (entry 6, 2a′): orange crystals ($CHCl_3$); mp 188–189 °C; IR (KBr) 2210 (CN) cm^{-1}; mass spectrum, m/e 304 (M^+), 243 (M – COS – H). Anal. Calcd for $C_{14}H_{12}N_2O_2S_2$: C, 55.24; H, 3.97; N, 9.20; S, 21.07. Found: C, 55.18; H, 3.88; N, 9.10; S, 20.99.

2-(p-Anisyl)-5-cyano-4-(ethylthio)-1,3-thiazin-6-one (entry 6, 3a): brown crystals (EtOH); mp 185–186° C; IR (KBr) 2210 (CN), 1640 (CO) cm^{-1}; mass spectrum, m/e 304 (M^+), 243 (M – COS – H).

5-Cyano-4-(ethylthio)-2-(p-nitrophenyl)-1,3-thiazin-6-one (entry 7, 3a′): orange crystals (EtOH); mp 203–204 °C; IR (KBr) 2210 (CN), 1640 (CO) cm^{-1}; mass spectrum, m/e 319 (M^+), 258 (M – COS – H). Anal. Calcd. for $C_{13}H_9N_3O_3S_2$: C, 48.89; H, 2.84; N, 13.16; S, 20.80. Found: C, 48.78; H, 2.80; N, 13.22; S, 20.13.

4-(Benzylthio)-5-cyano-2-(β-naphthyl)-1,3-thiazin-6-one (entry 8, 3a′): orange crystals EtOH); mp 216–217 °C; IR (KBr) 3050 (arom CH), 2200 (CN), 1650 (CO) cm^{-1}; mass spectrum, m/e 386 (M^+), 225 (M – COS – H). Anal. Calcd for $C_{22}H_{14}N_2OS_2$: C, 68.37; H, 3.65; N, 7.25; S, 16.59. Found: C, 68.25; H, 3.44; N, 7.30; S, 16.70.

2-(p-Anisyl)-4-(benzylthio)-5-cyano-1,3-oxazine-6-thione (entry 9, 2a′): orange crystals ($CHCl_3$); mp 181–182 °C; IR (KBr) 2210 (CN) cm^{-0}; mass spectrum, m/e 366 (M^+), 305 (M – COS – H). Anal. Calcd for $C_{19}H_{14}N_2O_2S_2$: C, 62.27; H, 3.85; N, 7.64; S, 17.50. found: C, 62.40; H, 3.90; N, 7.73; S, 17.77.

4-(Benzylthio)-5-cyano-2-phenyl-1,3-thiazin-6-one (entry 10, 3a′); yellow needles (AcOH); mp 196–197 °C; IR (KBr) 2210 (CN), 1630 (CO) cm^{-1}; NMR (Py-d_5) δ 8.15 (m, 2, Ph), 7.50 (m, 8 H, Ph), 4.80 (s, 2, CH_2); mass spectrum, m/e 336 (M^+), 275 (M – COS – H). Anal. Calcd for $C_{18}H_{12}N_2OS_2$: C, 64.26; H, 3.60; N, 8.33; S, 19.06. Found: C, 64.12; H, 3.67; N, 8.27; S, 19.22.

4-Benzyl-5-cyano-2-(p-nitrophenyl)-1,3-thiazin-6-one (entry 11, 3a′): orange crystals (EtOH); mp 188–190 °C; IR (KBr) 2210 (CN), 1650 (CO) cm^{-1}; mass spectrum, m/e 381 (M^+), 320 (M – COS – H). Anal. Calcd for $C_{18}H_{11}N_3O_3S_2$: C, 56.68; H, 2.91; N, 11.02; S, 16.81. Found: C, 56.79; H, 3.04; N, 11.10; S, 16.93.

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5-Cyano-2-phenyl-4-(phenylthio)-1,3-oxazine-6-thione (entry 12, 2a′): yellow needles (AcOEt); mp 199–200 °C; IR (KBr) 3030 (arom CH), 2210 (CN) cm^{-1}; NMR ($CDCl_3$) δ 7.95 (m, 2, pH), 7.65 (m, 8, Ph, SPh); mass spectrum, *m/e* 322 (M^+), 261 (M − COS −H). Anal. Calcd for $C_{17}H_{10}N_2OS_2$: C, 63.33; H, 3.13; N, 8.69; S, 19.90. Found: C, 63.03; H, 3.23; N, 8.55; S, 20.20.

Registry No. **1a**, 37614-61-2; **1a***, 87740-50-9; **1a**-d_3, 87740-51-0; **1a′** (R^1 = Et), 87740-52-1; **1a′** (R^1 = CH_2Ph), 65882-52-2; **1a′** (R^1 = Ph), 87740-53-2; **1b**, 87740-54-3; **1c**, 87740-55-4; **1d**, 57280-03-2; **1e**, 87740-56-5; **1f**, 87740-57-6; **1g**, 87740-58-7; **2a**, 80532-88-3; **2a***, 87740-59-8; **2a**-d_3, 87740-60-1; **2a′** (R^1 = Me; R^2 = β-naphthyl), 87740-61-2; **2a′** (R^1 = Me; R^2 = *p*-anisyl), 87740-62-3; **2a′** (R^1 = Me; R^2 = *o*-iodophenyl), 87740-63-4; **2a′** (R^1 = Et; R^2 = *p*-anisyl), 87740-64-5; **2a′** (R^1 = CH_2Ph; R^2 = *p*-anisyl), 87740-65-6; **2a′** (R^1 = R^2 = Ph), 87740-66-7; **3a**, 80532-90-7; **3a***, 87740-67-8; **3a**-d_3, 87740-68-9; **3a′** (R^1 = Me; R^2 = β-naphthyl), 87740-69-0; **3a′** (R^1 = Me; R^2 = *p*-anisyl), 87740-70-3; **3a′** (R^1 = Me; R^2 = *p*-chlorophenyl), 87740-71-4; **3a′** (R^1 = Me; R^2 = *o*-iodophenyl), 87740-72-5; **3a′** (R^1 = Me; R^2 = *p*-nitrophenyl), 87761-65-7; **3a′** (R^1 = Et; R^2 = *p*-anisyl), 87740-73-6; **3a′** (R^1 = Et; R^2 = *p*-nitrophenyl), 87740-74-7; **3a′** (R^1 = CH_2Ph; R^2 = β-naphthyl), 87740-75-8; **3a′** (R^1 = CH_2Ph; R^2 = Ph), 87740-76-9; **3a′** (R^1 = CH_2Ph; R^2 = *p*-nitrophenyl), 87740-77-0; **4a**, 80532-91-8; **4a***, 87740-78-1; **5a**, 80532-87-2; **5b**, 87740-79-2; **5c**, 87740-80-5; **5d**, 87740-81-6; **5e**, 87740-82-7; **5f**, 87740-83-8; **6a**, 87740-84-9; **6b**, 87740-85-0; methyl trithiocarbonate, 1113-26-4; cyanoacetamide, 107-91-5; *N*-methylcyanoacetamide, 6330-25-2; *N*-ethylcyanoacetamide, 15029-36-4; ethyl trithiocarbonate, 1118-64-5; methyl dithiopropionate, 5415-95-2; methyl dithiobenzoate, 2168-78-7; benzoic acid, 65-85-0; β-naphthoic acid, 93-09-4; *p*-methoxybenzoic acid, 100-09-4; *p*-chlorobenzoic acid, 74-11-3; o-iodobenzoic acid, 88-67-5; *p*-nitrobenzoic acid, 62-23-7.

Supplementary Material Available: ^{13}C NMR spectra of **4a** and **4a*** in Me_2SO-d_6 (67.8 MHz) with completely coupled and off-resonance decoupled protons (2 pages). Ordering information is given on any current masthead page.

Evidence against 1,2-Migrations in Aryl Cations

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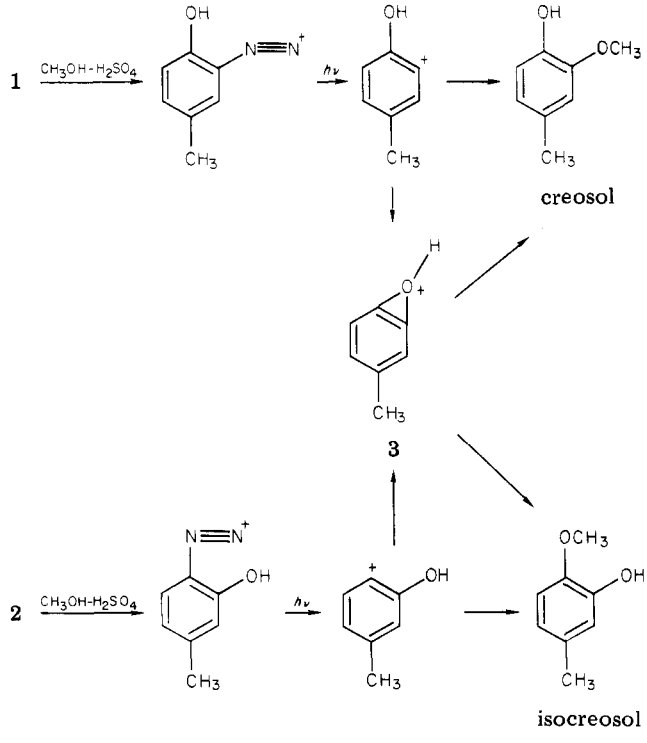
Photolytic methoxydediazoniation of 2-diazo-4-methylphenol (**1**) and 2-diazo-5-methylphenol (**2**) in 50% CH_3OH–H_2SO_4 yielded 2-methoxy-4-methylphenol (creosol) and 2-methoxy-5-methylphenol (isocreosol), respectively. The absence of detectable amounts of crossover products (within the limits of detection of 5%) in both reactions demonstrates that no 1,2-hydroxyl shift occurred in the intermediate phenylium ion nor could the hypothetical protonated benzoxirene be an intermediate in this reaction.

The dediazoniation reaction of arenediazonium ions is regarded as the one instance where a phenyl cation is a reaction intermediate.[1,2] One may reasonably ask whether there exists in the chemistry of the phenylium ion any behavior analogous to the widespread propensity to neighboring group effects among alkyl cations.[3,4]

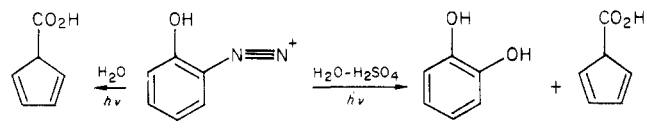
Participation by neighboring hydroxyl to form an epoxide is known in aliphatic chemistry[5] both in the case of dediazoniation[6] and in the case of carbonium ions generated from 1,2 diols,[7] although the major products in most of these cases arise from pinacol–pinacolone type rearrangements.

The formation of a bridged intermediate such as **3** suffers from several difficulties (Scheme I). First, the formation of epoxides, via aliphatic cations has, whenever studied,[8] required an anti-periplanar arrangement of the leaving group and the migrating group, which is of course not possible in the formation of **3**. The intermediate **3** would also suffer from the fact that it is the protonated form of a benzoxirene, an antiaromatic species. There is

Scheme I



Scheme II



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