

Preparation of New Nitrogen-Bridged Heterocycles. 28.¹⁾ First Syntheses of 1,3-Oxazino[6,5-*b*]indolizine Derivatives

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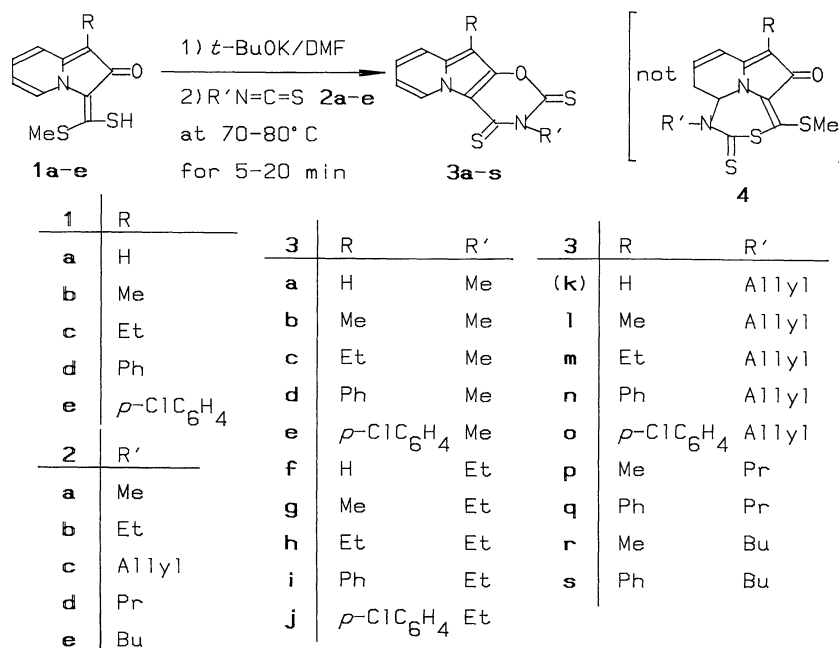
The reactions of 2-[mercapto(methylthio)methylene]-2(3*H*)-indolizinones with alkyl isothiocyanates in the presence of potassium *t*-butoxide in *N,N*-dimethylformamide afforded new heterocycles, 3-alkyl-2*H*-1,3-oxazino[6,5-*b*]indolizine-2,4(3*H*)-dithione derivatives, in moderate yields. On the other hand, their reactions with phenyl isothiocyanate did not afford the corresponding 2*H*-1,3-oxazino[6,5-*b*]indolizine-2,4(3*H*)-dithiones, although the reaction of 2-[mercapto(methylthio)methylene]-1-methyl-2(3*H*)-indolizinone with phenyl isothiocyanate gave 10-methyl-3-phenyl-2-phenylimino-2,3-dihydro-4*H*-1,3-oxazino[6,5-*b*]indolizine-4-thione in a very low yield (10%). The structures of these 2*H*-1,3-oxazino[6,5-*b*]indolizine-2,4(3*H*)-dithiones and the 2-phenylimino analogue were determined by inspections of their physical and spectral data and by a single crystal X-ray analysis of one of these compounds.

In previous work, we have documented that 3-(mercaptomethylene)-2(3*H*)-indolizinones reacted with some (acyl- or cyano-substituted)methyl halides in the presence of a base to give the corresponding new heterocycles, 8,8a-dihydro[1,4]thiazino[3,4,5-*cd*]indolizin-4(1*H*)-ones, which were formed via the smooth intramolecular Michael addition of the resulting *S*-alkylated products.²⁾ The high nucleophilicity of the mercapto group in these molecules^{2,3)} and our recent success in the preparation of 2*H*-1,3-thiazino[6,5-*b*]indolizine derivatives from potassium 2-indolizinethiolates¹⁾ prompted us to examine the reactions between these molecules and electron-poor heterocumulenes such as isocyanate and isothiocyanate. In contrast with the smooth *S*-alkylations of 3-(mercaptomethylene)-2(3*H*)-indolizinones, their reactions with alkyl or aryl isocyanates and isothiocyanates did not proceed under ordinary reaction conditions. They reacted only with isothiocyanates under more forceful conditions in the presence of a strong base, but the products were not the initially expected 5*H*-[1,3,5]thiadiazepino[6,5,4-*cd*]indolizine derivatives. In this paper we wish to report the first synthesis of 2*H*-1,3-oxazino[6,5-*b*]indolizine derivatives by the reactions of 3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinones with some isothiocyanates in the presence of a strong base.

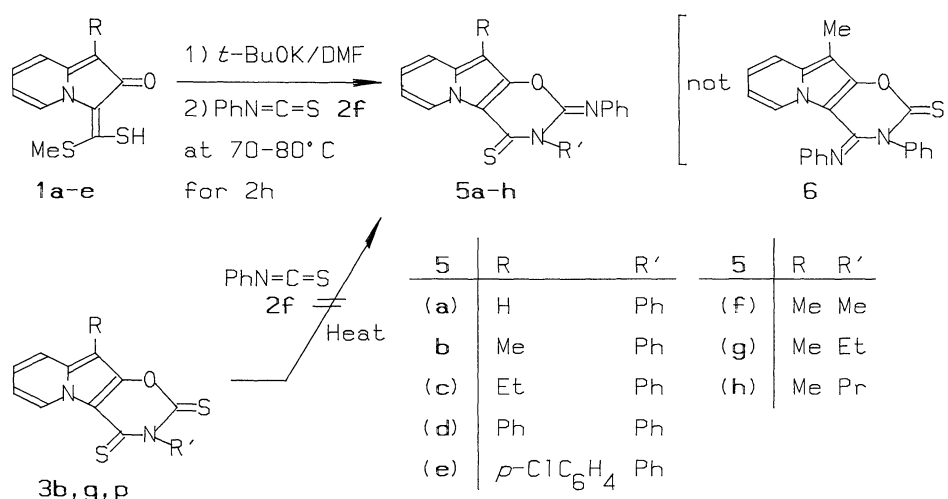
Results and Discussion

Reactions of 3-[Mercapto(methylthio)methylene]-2(3*H*)-indolizinones with Some Isothiocyanates. Since the high reactivity of the mercapto group of 3-(mercaptomethylene)-2(3*H*)-indolizinone derivatives toward various alkylating agents in the presence of a base was clearly shown,^{2,3)} their reactions with unsaturated electrophiles such as isocyanates and isothiocyanates were initially expected to form the corresponding 5*H*-

[1,3,5]thiadiazepino[6,5,4-*cd*]indolizine derivatives such as **4** (see Scheme 1) via the electrophilic attack of the reagent on the sulfur atom followed by the Michael addition of the resulting aminide ion to the 5-position on the indolizine ring. Hence, the reactions of 3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinones (**1a—e**), readily available from the alkaline treatment of 2-(substituted methyl)pyridinium bromides, carbon disulfide, and dimethyl sulfate,³⁾ with some isocyanates and isothiocyanates were examined carefully under various reaction conditions, and we found that, although their reactions with isocyanates did not provide any significant products, those with isothiocyanates afforded significant amounts of products when a strong base, potassium *t*-butoxide, was present. The structures of the products, however, were different from the expected ones (**4**) (See below). When a mixture of 2(3*H*)-indolizinone **1a—e**, methyl isothiocyanate (**2a**), and potassium *t*-butoxide was allowed to react in DMF at 70—80 °C for 20 min, the title compounds, 3-methyl-2*H*-1,3-oxazino[6,5-*b*]indolizine-2,4(3*H*)-dithiones **3a—e**, were obtained in 10—77% yields as orange crystals. Similar reactions of **1a—e** with ethyl isothiocyanate (**2b**), allyl isothiocyanate (**2c**), propyl isothiocyanate (**2d**), and butyl isothiocyanate (**2e**) in the presence of potassium *t*-butoxide gave the corresponding crystalline products **3f—j**, **1—s** except **3k**, in moderate yields. These results are shown in Scheme 1. On the other hand, the reaction of 2(3*H*)-indolizinone **1b** with phenyl isothiocyanate (**2f**) in the presence of potassium *t*-butoxide at 70—80 °C for 2 h provided an alternative product, 10-methyl-3-phenyl-2-phenylimino-2,3-dihydro-4*H*-1,3-oxazino[6,5-*b*]indolizine-4-thione **5a**, in a low yield (10%). The reactions of **1a**, **c—e** with the same reagent **2f** did not give any products. Furthermore, the type of product such as **5f—h** could not be obtained by the reactions of 2*H*-1,3-



Scheme 1.



Scheme 2.

oxazino[6,5-*b*]indolizine-2,4(3*H*)-dithione (**3b**, **g**, **p**) with **2f**. (Scheme 2)

As described above, the structures of compounds **3a**—**s** were first considered to be 5*H*-[1,3,5]thiadiazepino[6,5,4-*cd*]indolizin-5-one derivatives such as **4**, but their ¹H NMR (see Table 1) and mass spectra and elemental analyses clearly excluded this structure. For example, the ¹H NMR spectrum of compound **3a** showed only the signals due to the aromatic indolizine ring protons (δ =10.64 (1H, br d, *J*=7.0 Hz, 6-H), 7.2–7.7 (2H, m, 8-H and 9-H), 7.00 (1H, m, 7-H), and 6.25 (1H, s, 10-H)) and the *N*-methyl protons (δ =4.23 (3H, s)); any other signals attributable to the methylthio group were not present. The ¹H NMR spectra of the products **3a**—**j**,

l—**s** were very similar to each other, and the mass spectra of **3a**, **b**, **d** and elemental analyses of **3a**—**j**, **l**—**s** were also in good accord with the proposed structures.

Furthermore, the X-ray analysis of a single crystal of 3,10-dimethyl-2*H*-1,3-oxazino[6,5-*b*]indolizine-2,4(3*H*)-dithione (**3b**) was performed and its structure was confirmed. The single crystal of this molecule **3b** was grown from an ethanolic solution. An orange monoclinic crystal for **3b** was used. Crystal data and details of the structure analysis are shown in Tables 2 and 3.⁴⁾ The ORTEP⁵⁾ drawing is shown in Fig. 1.

On the other hand, the structure of product **5b** was determined by elemental analysis and by spectral comparison with those of the 2*H*-1,3-oxazino[6,5-*b*]-

Table 1. ^1H NMR Spectral Data of 2*H*-1,3-Oxazino[6,5-*b*]indolizines

No ^{a)}	C-6	C-7	C-8	C-9	C-10	R
3a	10.64 br d	7.00 m	7.2—7.7 m		6.25 s	4.23 s
3b	10.63 br d	6.93 m	7.3—7.7 m		2.34 s	4.24 s
3c	10.52 br d	6.95 dt	7.1—7.7 m		1.26 2.80 t q	4.18 s
3d	10.77 br d	7.05 dt	b)	7.87 br d	7.2—7.8 m	4.25 s
3e	10.72 br d	7.06 dt	b)	7.83 br d	7.2—7.8 m	4.24 s
3f	10.60 br d	7.00 m	7.2—7.7 m		6.22 s	1.44 5.10 t q
3g	10.58 br d	7.00 dt	7.3—7.7 m		2.33 s	1.45 5.12 t q
3h	10.58 br d	6.95 dt	7.2—7.7 m		1.29 2.80 t q	1.40 5.08 t q
3i	10.78 br d	7.06 dt	b)	7.88 br d	7.2—7.8 m	1.46 5.13 t q
3j	10.50 br d	7.05 dt	b)	7.82 br d	7.2—7.8 m	1.42 5.14 t q
3l	10.53 br d	6.95 dt	7.1—7.7 m		2.32 s	5.0—6.5 m
3m	10.62 br d	6.98 dt	7.1—7.7 m		1.26 2.80 t q	5.0—6.5 m
3n	10.73 br d	7.03 dt	b)	7.87 br d	7.2—7.8 m	5.0—6.5 m
3o	10.72 br d	7.05 dt	b)	7.83 br d	7.2—7.8 m	5.0—6.5 m
3p	10.54 br d	6.95 dt	7.2—7.7 m		2.27 s	0.99 1.4—2.2 4.89 t m br t
3q	10.71 br d	7.02 dt	b)	7.84 br d	7.2—7.8 m	1.01 1.4—2.2 4.93 t m br t
3r	10.59 br d	6.96 dt	7.2—7.7 m		2.29 s	0.98 1.1—2.2 4.97 t m br t
3s	10.70 br d	7.01 dt	b)	7.83 br d	7.2—7.8 m	0.99 1.1—2.2 4.99 t m br t
5b	10.57 br d	b)	b)	b)	2.16 s	6.7—7.7 m

a) The coupling constants were as follows: $J_{6,7}=J_{7,8}=7.0$, $J_{8,9}=9.0$, $J_{6,8}=2.0$, and $J_{Et}=7.0$ Hz. b) Overlapped with the phenyl proton signals.

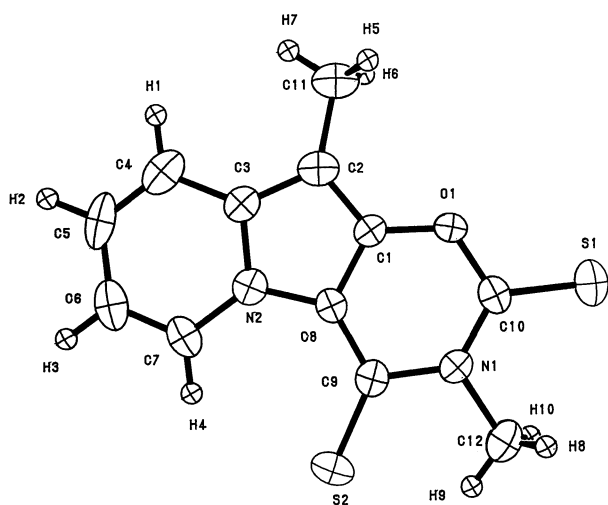


Fig. 1. ORTEP drawing of 3,10-dimethyl-2*H*-oxazino[6,5-*b*]indolizin-2,4(3*H*)-dithione (**3b**) showing the atom labeling scheme and 50% probability thermal ellipsoids.

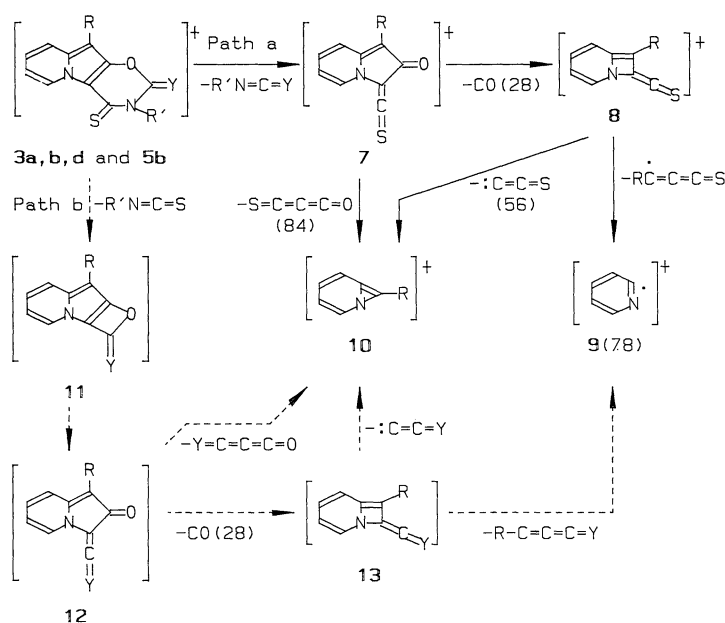
indolizine-2,4(3*H*)-dithiones **3**. The mass spectrum (M^+ 383) and the elemental analysis of **5b** showed that the molecular formula was $\text{C}_{23}\text{H}_{17}\text{N}_3\text{OS}$ which corresponded to the subtraction of one mole of carbon disulfide from the 1:2 adduct between indolizine **1b** and phenyl isothiocyanate (**2f**). The structural formula presumed from these findings and the mechanistic considerations was either 10-methyl-3-phenyl-2-phenylimino-2,3-dihydro-4*H*-1,3-oxazino[6,5-*b*]indolizine-4-thione **5b** or an alternative 4-phenylimino derivative **6**. The largely deshielded chemical shift ($\delta=10.57$) attributable to the 6-*H* proton in **5b** was very similar to those ($\delta=10.53$ — 10.78) of **3a**—**j**, **l**—**s**, indicating the similarity of the magnetic circumstances between them. Furthermore, the interpretation of the fragmentations in the mass spectra of **5b** and **3a,b,d** confirmed the structure of **5b**: The mass spectrum of **5b** exhibited m/z 383 (21%, M^+), 248 (13%, $M^+ - \text{PhN}=\text{C}=\text{S}$), 189 (100%, $M^+ - \text{PhN}=\text{C}=\text{NPh}$), 161 (3%, $M^+ - 222$), 105 (13%, $M^+ - 278$), and 78 (4%,

Table 2. Crystal and Structure Analysis Data of Compound **3b**

3b	
Formula	C ₁₂ H ₁₀ N ₂ OS ₂
Formula weight	262.34
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>m</i> ; <i>Z</i> =2
Lattice parameters	
<i>a</i> /Å	9.094 (4)
<i>b</i> /Å	6.731 (4)
<i>c</i> /Å	9.859 (2)
β /°	103.47 (2)
<i>V</i> /Å ³	586.9 (4)
<i>D</i> _{calcd} /g cm ⁻³	1.484
Crystal size/mm ³	0.08×0.04×0.80
Diffractometer	Rigaku AFC5S
Radiation	MoK α (λ =0.71069 Å)
Monochromator	Graphite
Scan type	ω -2 θ
2 θ Max	55.0°
Computer program	TEXSAN System ^{a)}
Structure solution	Direct method; MITHRIL ^{b)}
Hydrogen atom treatment	Calculated, not refined
Refinement	Full-matrix, anisotropic
Least-squares weight	4 <i>F</i> _o ² / σ ² (<i>F</i> _o ²)
No. of measurement ref.	Total: 4311, Unique: 4017
No. of observations ^{c)}	707
No. of variables	103
Residuals <i>R</i> ; <i>R</i> _w	0.072; 0.107
Max Shift/Error	0.02
$\Delta\rho_{\max}$ /e ⁻ Å ⁻³	0.45

a) See Ref. 6. b) See Ref. 10. c) $I < 3.00\sigma(I)$.Table 3. Atomic Coordinates (×10³) and Equivalent Temperature Factors of Compound **3b** (esd's, where given, are in parentheses)

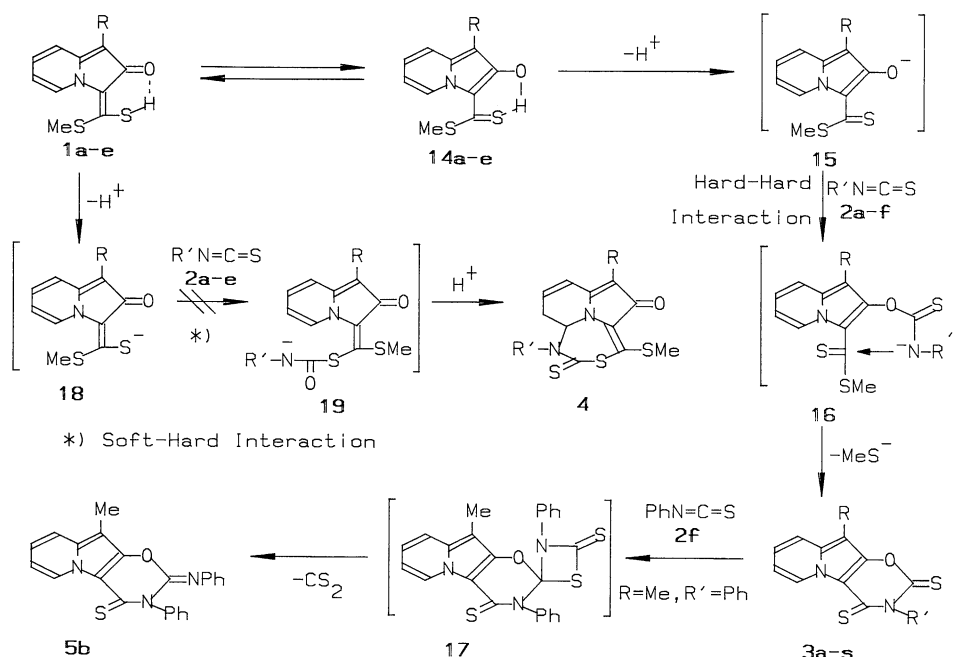
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} ^{a)} /Å ²
S1	-64.9 (4)	1/4	200.1 (4)	4.4 (2)
S2	509.1 (4)	1/4	149.5 (4)	4.3 (2)
O1	161.7 (8)	1/4	407.4 (8)	2.6 (4)
N1	228 (1)	1/4	194 (1)	2.7 (4)
N2	559 (1)	1/4	495 (1)	2.6 (4)
C1	310 (1)	1/4	473 (1)	2.5 (5)
C2	372 (1)	1/4	613 (1)	3.1 (6)
C3	529 (1)	1/4	627 (1)	2.6 (5)
C4	654 (2)	1/4	743 (2)	4.1 (7)
C5	795 (2)	1/4	725 (2)	4.3 (7)
C6	821 (1)	1/4	589 (2)	4.1 (7)
C7	706 (1)	1/4	478 (2)	3.4 (6)
C8	423 (1)	1/4	396 (1)	2.3 (5)
C9	387 (1)	1/4	250 (1)	3.1 (6)
C10	118 (1)	1/4	268 (1)	2.8 (6)
C11	292 (2)	1/4	729 (1)	4.1 (7)
C12	181 (2)	1/4	40 (2)	6(1)
H1	636.0	1/4	834.0	5.0
H2	878.2	1/4	804.4	5.2
H3	921.4	1/4	577.2	5.0
H4	723.8	1/4	386.0	4.0
H5	228.6	365.2	721.4	4.9
H6	228.6	134.8	721.4	4.9
H7	361.7	1/4	815.6	4.9
H8	117.8	364.1	9.2	7.6
H9	264.5	252.3	0.3	7.6
H10	120.7	133.6	9.0	7.6

a) $B_{eq} = \frac{8\pi^2}{3} \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Scheme 3.

M⁺—305), and those of **3a, b, d** showed definite peaks due to the corresponding M⁺, (M⁺—MeN=C=S), (M⁺—101), (M⁺—157), and 78 ions, respectively. The possible fragmentation patterns of the molecules **3a, b, d**, and **5b**

are illustrated in Scheme 3. Although respective ions can be generally derived from both Path a (solid line) and Path b (dashed line), Path a is energetically more favorable than Path b because the fissions of any bonds



Scheme 4.

connected with the aromatic indolizine ring are not involved in this route.⁶⁾ The predominance of the m/z 189 ion ($M^+ - \text{PhN}=\text{C}=\text{NPh}$) over the m/z 248 ion ($M^+ - \text{PhN}=\text{C}=\text{S}$) strongly supported that this product was **5b** but not **6**.

Reaction Mechanisms. The formation of the 3-alkyl-2*H*-1,3-oxazino[6,5-*b*]indolizine-2,4(3*H*)-dithiones (**3a—j, l—s**) were explained by the initial abstraction of the active hydrogen in 3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinones **1a—e** or their 2-hydroxy tautomers **14a—e** with potassium *t*-butoxide, the electrophilic addition of isothiocyanate **2** to the resulting 2-indolizineolate ions **15**, and by the intramolecular nucleophilic attack of the aminide ion **16** to the thiocarbonyl carbon at the 3-position followed by the elimination of a methylthio anion. This mechanism is very similar to those proposed for the syntheses of 2*H*-1,3-benzoxazine-2-thiones⁷⁾ and 2*H*-1,3-thiazino[6,5-*b*]indolizin-2-thiones.¹⁾ The reason why the initially expected product **4** could not be formed by the reaction between the alternative thiolate ion **18** and isothiocyanate **2** may be explained by considering the unfavorable interaction between this anion **18** and reagents **2** based on a HSAB principle.⁸⁾ On the other hand, 2-phenylimino derivative **5b** must be formed via the [2+2] cycloaddition of phenyl isothiocyanate (**2f**) to 10-methyl-3-phenyl-2*H*-[1,3]oxazino[6,5-*b*]indolizine-2,4(3*H*)-dithione once formed followed by the cycloreversion of the 2*H*-1,3-thiazetidine-2-thione ring in the resulting **17** with the elimination of carbon disulfide. However, the reason why other compounds **5a, c—h** could not be obtained by similar reactions of **1a, c—e** and

3b,g,p with **2f** is still unclear. These mechanism are summarized in Scheme 4.

Experimental

Melting points were measured with a Yanagimoto micromelting point apparatus and were not corrected. The microanalyses were carried out on a Perkin-Elmer 2400 elemental analyzer. The ¹H NMR spectra were determined with a Varian EM360A spectrometer in deuterochloroform with tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. The IR spectra were taken with a Hitachi 260-10 infrared spectrophotometer.

Preparations of 3-[Mercapto(methylthio)methylene]-2(3*H*)-indolizinones. The preparation of 3-[mercapto(methylthio)methylene]-1-phenyl-2(3*H*)-indolizinone **1d**, mp 121–122 °C (Lit.³⁾ mp 121–122 °C), was carried out according to our previous procedure, and those of **1a—c, e** by modified procedures: **General Method.** An ethanolic solution (100 ml) of 2-methyl-, 2-ethyl-, 2-propyl-, or 2-(*p*-chlorobenzyl)pyridinium bromide (10 mmol) was treated with ethanolic sodium ethoxide at room temperature for 15–20 min. Carbon disulfide (12 mmol) and then dimethyl sulfate (11 mmol) were added to the mixture and the resulting solution was stirred for an additional 20 min. The reaction mixture was poured into 300 ml of water and was extracted with two portions of chloroform (300 ml). The chloroform layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was chromatographed on a column of alumina using chloroform as an eluent to give the crude 2(3*H*)-indolizinone, which was recrystallized from ethanol (**1a,c**) or chloroform (**1b,e**).

Some data for new compounds are as follows: **1a**, 19% yield, orange needles, mp 128–131 °C, ν (KBr) 2570 (SH) and 1570 (CO) cm^{-1} , Anal. ($\text{C}_{10}\text{H}_9\text{NOS}_2$) C, H, N.

Table 4. Some Data of the 2*H*-1,3-Oxazino[6,5-*b*]indolizines

No ^{a)}	React	Yield %	Mp °C	ν (KBr) cm ⁻¹		Formula ^{b)}
3a	1a 2a	24	246—247	1560	1532	C ₁₁ H ₈ N ₂ OS ₂
3b	1b 2a	77	283—284	1590	1533	C ₁₂ H ₁₀ N ₂ OS ₂
3c	1c 2a	54	185—186	1580	1523	C ₁₃ H ₁₂ N ₂ OS ₂
3d	1d 2a	40	230—232	1566	1527	C ₁₇ H ₁₂ N ₂ OS ₂
3e	1e 2a	10	253—255	1569	1525	C ₁₇ H ₁₁ N ₂ OS ₂ Cl
3f	1a 2b	10	188—189	1560	1533	C ₁₂ H ₁₀ N ₂ OS ₂
3g	1b 2b	23	224—225	1589	1529	C ₁₃ H ₁₂ N ₂ OS ₂
3h	1c 2b	39	184—185	1581	1528	C ₁₄ H ₁₄ N ₂ OS ₂
3i	1d 2b	12	189—190	1581	1531	C ₁₈ H ₁₄ N ₂ OS ₂
3j	1e 2b	11	194—196	1570	1521	C ₁₈ H ₁₃ N ₂ OS ₂ Cl
3k	1a 2c	0				
3l	1b 2c	85	215—217	1587	1529	C ₁₄ H ₁₂ N ₂ OS ₂
3m	1c 2c	41	140—142	1584	1530	C ₁₅ H ₁₄ N ₂ OS ₂
3n	1d 2c	27	186—187	1570	1528	C ₁₉ H ₁₄ N ₂ OS ₂
3o	1e 2c	23	209—211	1571	1527	C ₁₉ H ₁₃ N ₂ OS ₂ Cl
3p	1b 2d	17	178—180	1590	1532	C ₁₄ H ₁₄ N ₂ OS ₂
3q	1d 2d	6	200—203	1569	1523	C ₁₉ H ₁₆ N ₂ OS ₂
3r	1b 2e	14	167—168	1591	1537	C ₁₅ H ₁₆ N ₂ OS ₂
3s	1d 2e	9	170—172	1568	1525	C ₂₀ H ₁₈ N ₂ OS ₂

a) All compounds were obtained as orange needles. b) Satisfactory analytical data (within 0.3% for C, H, and N) were obtained for all compounds.

1b, 65% yield, orange needles, mp 134—135 °C, ν (KBr) 2580 (SH) and 1588 (CO) cm⁻¹, Anal. (C₁₁H₁₁NOS₂) C, H, N.

1c, 30% yield, orange needles, mp 78—80 °C, ν (KBr) 2580 (SH) and 1585 (CO) cm⁻¹, Anal. (C₁₂H₁₃NOS₂) C, H, N.

1e, 71% yield, orange needles, mp 153—154 °C, ν (KBr) 2520 (SH) and 1585 (CO) cm⁻¹, Anal. (C₁₆H₁₂ClNOS₂) C, H, N.

Reactions of 2(3*H*)-Indolizinones with Alkyl Isothiocyanates. General Method. A DMF solution (1 ml) of 3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinone (**1**, 1 mmol) and isothiocyanate (**2**, 2 mmol) was treated with potassium *t*-butoxide (2 mmol) at 70—80 °C for 20 min. The reaction mixture was neutralized with diluted hydrochloric acid and then extracted with chloroform (20 ml). Water was removed from the chloroform solution by passage through phase-separating filter paper and the filtrate was concentrated under reduced pressure. The residue was separated by column chromatography on alumina using chloroform as an eluent. The chloroform solution was concentrated under reduced pressure and the recrystallization of the crude products from ethanol gave the corresponding 2*H*-1,3-oxazino[6,5-*b*]indolizine-2,4-dithione derivatives **3a—s** as orange needles. The results and some physical and spectral data of **3a—s** are listed in Tables 1 and 4.

The prolonged reactions (1—4 h) of indolizinones **1** and isothiocyanates **2** gave diminished yields of the products **3**.

Reaction of 1-Methyl-2(3*H*)-indolizinone 1b with Phenyl Isothiocyanate (2f). A DMF solution (1 ml) of **1b** (1 mmol) and **2f** (2 mmol) was heated at 70—80 °C for 2 h in the presence of potassium *t*-butoxide (2 mmol). The usual work-up of the resulting mixture gave 10-methyl-3-phenyl-2-phenylimino-2,3-dihydro-4*H*-1,3-oxazino[6,5-*b*]indolizine-4-thione (**5b**), 10% yield, orange needles, mp 266—268 °C, ν (KBr) 1675 (C=N) cm⁻¹, Anal. (C₂₃H₁₇N₃OS) C, H, N (See Table 1 for its ¹H NMR

spectrum)

On the other hand, the reactions of indolizinones **1a,c—e** and 2*H*-1,3-oxazino[6,5-*b*]indolizine-2,4(3*H*)-dithiones **3b,g,p** with phenyl isothiocyanate (**2f**) did not afford any significant products under various reaction conditions.

References

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