Preparation of New Nitrogen-Bridged Heterocycles. 46.[1] Selective Formation of 4(1*H*)-8,8a-Dihydro-1,4-thiazino[3,4,5-*cd*]indolizinone and (*E*)-3-(1,3-Oxathiol-2-ylidene)-2(3*H*)-indolizinone Derivatives

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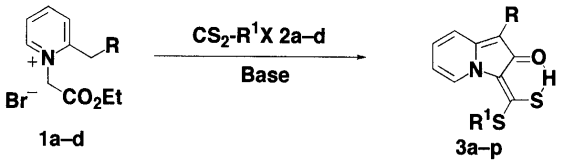
The reactions of (*Z*)-3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinones with bromoacetonitrile and bromoacetates in the presence of a base gave the corresponding 4(1*H*)-8,8a-dihydro-1,4-thiazino[3,4,5-*cd*]indolizinone derivatives, but similar treatment of the same compounds with some phenacyl bromides provided a quite different type of product, (*E*)-3-(5-aryl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinones, in 12—74% yield with the evolution of methanethiol. Interestingly, the reactions of (*Z*)-3-[mercapto(phenacylthio)methylene]-2(3*H*)-indolizinones and iodomethane in the presence of a base did not afford the expected (*Z*)-3-(5-aryl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinones, but gave only the same (*E*)-isomers in 22—53% yields. The stereochemistry about the C3–C2′ double bond in these 3-(5-aryl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinones was determined to be (*E*) by X-ray analysis.

Key words 3-(mercaptomethylene)-2(3*H*)-indolizinones; *S*-alkylation; cyclization; 3-(1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinones; 1,4-thiazino[3,4,5-*cd*]indolizine; X-ray analysis

It is well known that 2(3*H*)-indolizinones and related compounds are useful precursors for the preparation of some 2,3-fused and 3,5-fused indolizines.[2] The origin of their high versatility is largely owing to the presence of the trienone system in these molecules and their dihydroaromatic character. As a part of our studies directed toward the novel reactivity of this type of compound, we have already reported the formation of 4(1*H*)-8,8a-dihydro-1,4-thiazino[3,4,5-*cd*]-indolizinone derivatives from the alkaline treatment of (*Z*)-3-[alkyl- and aryl(mercapto)methylene]-2(3*H*)-indolizinones and various alkyl halides.[2e,f] However, we recently noticed that similar reactions of certain substrates such as 3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinones with phenacyl bromides afforded a quite different type of product. In this paper we report the selective formation of the title compounds from the reactions of (*Z*)-3-[mercapto(methylthio- and (*Z*)-3-[mercapto(phenacylthio)methylene]-2(3*H*)-indolizinones with some alkylating agents in the presence of a base.

Results and Discussion

Preparation of 3-[Mercapto(methylthio)- and (phenacylthio)methylene]-2(3*H*)-indolizinones These (*Z*)-3-[mercapto(methylthio- (**3a**—**d**) and (*Z*)-3-[mercapto(phenacylthio)methylene]-2(3*H*)-indolizinones (**3e**—**p**) were obtained as orange crystalline products from the reactions of 1-ethoxycarbonylmethyl-2-ethyl-, 2-propyl-, 2-benzyl-, and 2-(*p*-chlorobenzyl)pyridinium bromides (**1a**—**d**) with carbon disulfide and alkylating agents such as dimethyl sulfate (**2a**), phenacyl bromide (**2b**), *p*-chlorophenacyl bromide (**2c**), and *p*-bromophenacyl bromide (**2d**) in the presence of a base (Chart 1). The IR spectra of products **3a**—**p** showed the characteristic lowered carbonyl absorption band of 2(3*H*)-indolizinone derivatives at 1581—1598 cm^{-1} and a mercapto absorption band in the range of 2463—2633 cm^{-1}, and the UV spectra exhibited absorption maxima near 250, 300 (**3c**,



1	R
a	Me
b	Et
c	Ph
d	*p*-ClC$_6$H$_4$

2	R^{1}X
a	Me$_2$SO$_4$
b	PhCOCH$_2$Br
c	*p*-ClC$_6$H$_4$COCH$_2$Br
d	*p*-BrC$_6$H$_4$COCH$_2$Br

3	R	R^1
a	Me	Me
b	Et	Me
c	Ph	Me
d	*p*-ClC$_6$H$_4$	Me
e	Me	PhCOCH$_2$
f	Et	PhCOCH$_2$
g	Ph	PhCOCH$_2$
h	*p*-ClC$_6$H$_4$	PhCOCH$_2$

3	R	R^1
i	Me	*p*-ClC$_6$H$_4$COCH$_2$
j	Et	*p*-ClC$_6$H$_4$COCH$_2$
k	Ph	*p*-ClC$_6$H$_4$COCH$_2$
l	*p*-ClC$_6$H$_4$	*p*-ClC$_6$H$_4$COCH$_2$
m	Me	*p*-BrC$_6$H$_4$COCH$_2$
n	Et	*p*-BrC$_6$H$_4$COCH$_2$
o	Ph	*p*-BrC$_6$H$_4$COCH$_2$
p	*p*-ClC$_6$H$_4$	*p*-BrC$_6$H$_4$COCH$_2$

Chart 1

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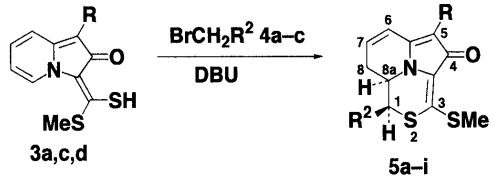
d, **g**, **h**, **k**, **l**, **o**, **p**) or 320 (**3a**—**c**, **e**, **f**, **j**, **k**, **m**, **n**), 400, and 450 nm, respectively.[3] The elemental analyses were also in good agreement with the compositions for our proposed structures. The (*Z*)-stereochemistry at the exocyclic methylene group at the 3-position in new compounds **3a**, **b**, **d**—**p** was determined by spectral comparison with the known product **3c**[2a] and also by the indication of the mercapto proton signal largely shifted to δ=12.22—13.22 ppm by the hydrogen-bonding with the 2-oxo group in the ^{1}H-NMR spectra.

Reactions of 3-(Mercaptomethylene)-2(3*H*)-indolizinones with Various Alkyl Halides Although no significant product could be isolated from the reactions of (*Z*)-3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinones (**3a**, **d**) with bromoacetonitrile (**4a**) in the presence of 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), similar treatment of **3a**, **c**, **d** with bromoacetonitrile (**4a**), ethyl bromoacetate (**4b**), or *tert*-butyl bromoacetate (**4c**) afforded the corresponding 4(1*H*)-8,8a-dihydro-1,4-thiazino[3,4,5-*cd*]indolizinone derivatives (**5b**, **d**—**l**) in 13—43% yields (Chart 2).

On the other hand, the reactions of (*Z*)-3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinones (**3a**—**d**) with phenacyl bromide (**2b**), *p*-chlorophenacyl bromide (**2c**), and *p*-bromophenacyl bromide (**2d**) in the presence of DBU did not provide the initially expected 1-arylcarbonyl-4(1*H*)-8,8a-dihydro-1,4-thiazino[3,4,5-*cd*]indolizinone derivatives such as **5** at all. In these reactions (*E*)-3-(5-aryl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinone derivatives (**6a**—**l**) were isolated in 12—74% yields. Similar reactions of (*Z*)-3-[mercapto(phenacylthio)methylene]-2(3*H*)-indolizinones (**3e**—**p**) with iodomethane (**2e**) were examined in expectation of the formation of (*Z*)-3-(5-aryl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinones (**7**), but only the same products **6a**—**l** were obtained in 22—50% yields (Chart 3). In these reactions the evolution of methanethiol was also confirmed by its strong odor.

The structures of 4(1*H*)-8,8a-dihydro-1,4-thiazino[3,4,5-*cd*]indolizinone derivatives (**5b**, **d**—**l**) were determined mainly by the comparison of their physical and spectral data with those of similar type of compounds prepared earlier by us.[2e,f] In particular, the presence of the singlet signal near δ=2.5 ppm due to the 3-methylthio group and of the doublet signal (its coupling constant is 2.0 Hz) coupled with the 8a-proton at δ=4.0—4.2 ppm due to the 1-proton in the ^{1}H-NMR spectra of **5b**, **g**—**l** made the structures clear. The UV spectra of **5b**, **d**—**l** showed absorption maxima near 250, 290, 370, and 480 nm, and the longest absorption maximum was longer than that of 3-methylene-2(3*H*)-indolizinones **3a**—**p**.[4] The structures for products **5d**—**f** whose signal due to the 1-proton overlapped with the methylene signals of the 1-ethoxycarbonyl group were determined by the analogy to these reactions.

On the other hand, the structures of another type of product **6a**—**l** were presumed by spectral inspection and finally determined by a X-ray analysis for compound **6a**. The elemental analyses of products **6a**—**l** were in good accord with our proposed compositions, and their UV spectra exhibited the longest absorption maxima near 500 nm, indicating the extension of the conjugated system. The ^{1}H-NMR spectra did not show any signal due to the methylthio group. These findings were fully consistent with our experimental observation in which these reactions proceeded with the elimination of methanethiol. Furthermore, the presence of the proton signals attributable to the 2(3*H*)-indolizinone moiety and the appearance of a new singlet signal (4′-H) appearing in the olefinic region (near δ=6.9) in the ^{1}H-NMR spectra strongly

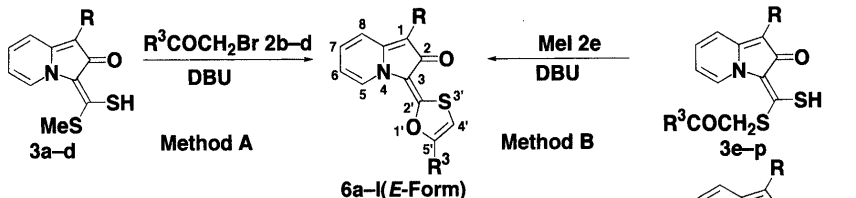


3a,c,d 5a–i

4	R^2
a	CN
b	CO_2Et
c	CO_2*tert*-Bu

5	R	R^2	Yield(%)
(a)	Me	CN	0
b	Ph	CN	13
(c)	*p*-ClC_6H_4	CN	0
d	Me	CO_2Et	22
e	Ph	CO_2Et	36
f	*p*-ClC_6H_4	CO_2Et	42
g	Me	CO_2*tert*-Bu	31
h	Ph	CO_2*tert*-Bu	37
i	*p*-ClC_6H_4	CO_2*tert*-Bu	43

Chart 2



6	R	R^2	Method(%) A	B
a	Me	Ph	43	33
b	Me	*p*-ClC_6H_4	38	50
c	Me	*p*-BrC_6H_4	46	23
d	Et	Ph	32	29
e	Et	*p*-ClC_6H_4	17	31
f	Et	*p*-BrC_6H_4	12	50

6	R	R^2	Method(%) A	B
g	Ph	Ph	74	48
h	Ph	*p*-ClC_6H_4	65	53
i	Ph	*p*-BrC_6H_4	68	38
j	*p*-ClC_6H_4	Ph	19	27
k	*p*-ClC_6H_4	*p*-ClC_6H_4	34	22
l	*p*-ClC_6H_4	*p*-BrC_6H_4	28	35

Chart 3

indicated the formation of a 1,3-oxathiole ring *via* the intramolecular cyclization of a possible reaction intermediate (see mechanisms). However, we could not decide the configuration about the 3-carbon-2′-carbon double bond in **6a**—**l** from only these spectral data. Finally, the configuration about this double bond was determined to be (*E*) by the X-ray analysis of product **6a**. The ORTEP drawing[5] for **6a** is shown in Fig. 1. The bond lengths between the 2′-carbon and the 1′-oxygen atoms and between the 2′-carbon and 3′-sulfur atoms were 1.357(4) and 1.729(4) Å, respectively, and these values are fairly shorter than the bond lengths for normal carbon–oxygen and carbon–sulfur single bonds. This fact shows that these bonds have some extent of double-bond character.

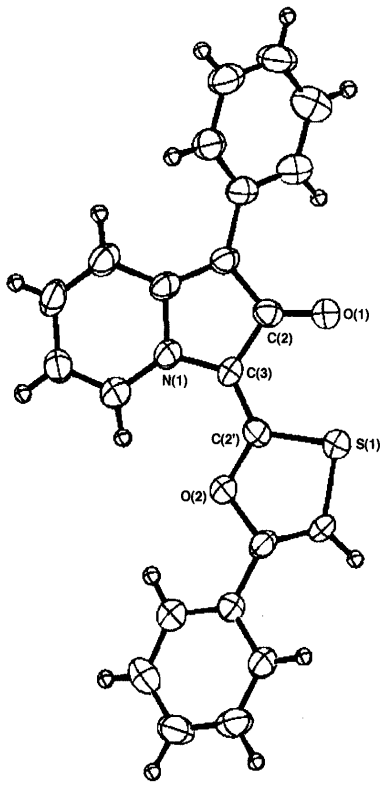


Fig. 1. ORTEP Drawing of 1-Phenyl-(*E*)-3-(5-phenyl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinone (**6a**)

Reaction Mechanisms Since the reaction routes from some (*Z*)-3-[mercaptomethylene]-2(3*H*)-indolizinones and similar alkylating agents to the corresponding 4(1*H*)-8,8a-dihydro-1,4-thiazino[3,4,5-*cd*]indolizinone derivatives such as **5** were already discussed in our previous papers,[2e,f] we describe here the reaction mechanisms (see Chart 4) for the formation of (*E*)-3-(5-aryl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinone derivatives (**6a**—**l**). Mechanistically, the *S*-alkylation of (*Z*)-3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinones (**3a**—**d**) with phenacyl bromides (**2b**—**d**), the deprotonation from the active methylene group in the resulting (*Z*)-3-[(methylthio(phenacylthio)methylene]-2(3*H*)-indolizinones (**8**), followed by the intramolecular nucleophilic substitution of the enolate anion **9′** would provide **6a**—**l** with the elimination of methanethiol (Path A). On the other hand, the reactions of (*Z*)-3-[mercapto(phenacylthio)-methylene]-2(3*H*)-indolizinones (**3e**—**p**) with iodomethane (**2e**) should afford (*Z*)-3-(5-aryl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinone derivatives (**7**) *via* a similar reaction manner (Path B), but the products actually obtained were the (*E*)-isomers (**6a**—**l**). Apparently, *cis–trans* isomerzation at the 3-exomethylene group in the indolizinone skeleton must take place during these reactions. Since the carbon–carbon double bond in β,β-bis(alkylthio)enone is strongly polarized and we previously observed a smooth *cis–trans* isomerization from (*E*)-3-[alkyl- or aryl(substituted methylthio)methylene]-2(3*H*)-indolizinones to the corresponding (*Z*)-isomers,[2f] both the *cis–trans* isomerizations from 3-[bis(alkylthio)methylene]-2(3*H*)-indolizinones (**10**) to **8** and from (*Z*)-3-(5-aryl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinone derivatives (**7**) to (*E*)-isomers **6a**—**l** are possible.

The reason why both reactions of (*Z*)-3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinones (**3a**—**d**) with phenacyl bromides **2b**—**d** and of (*Z*)-3-[mercapto(phenacylthio)methylene]-2(3*H*)-indolizinones (**3e**—**l**) with iodomethane (**2e**) did not provide 4(1*H*)-8,8a-dihydro-1,4-thiazino[3,4,5-*cd*]indolizinone derivatives such as **5** is unclear. However, the higher electrophilicity at the 3(1)-position in bis(alkylthiomethylene)-2(3*H*)-indolizinone skeleton and the stabiliza-

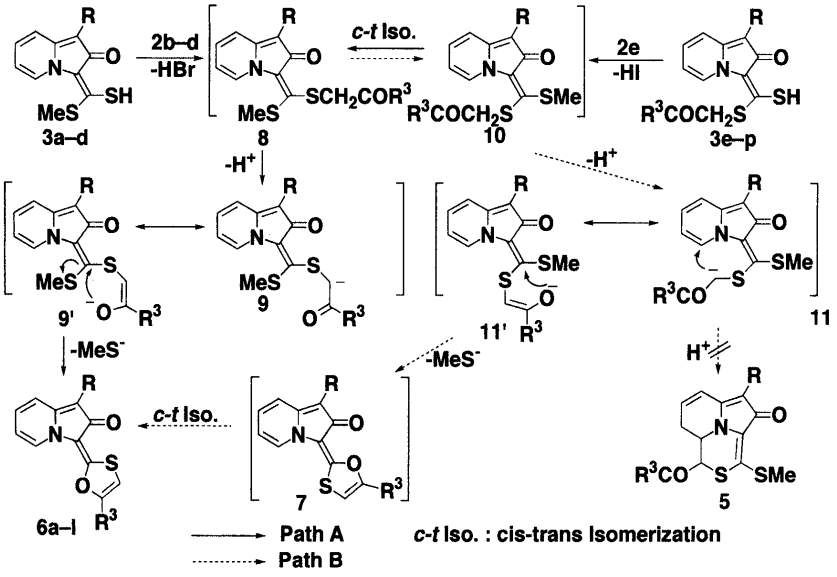


Chart 4

tion of the products **6a**—**l** due to the formation of the 1,3-oxathiole ring with a partial aromaticity as shown in the shortened bond lengths of the 1′–2′ and 2′–3′ bonds in the 1,3-oxathiole ring may be considered as reasons for it.

Experimental

Melting points were measured with a Yanagimoto micromelting point apparatus and were not corrected. Microanalyses were carried out on a Perkin-Elmer 2400 elemental analyzer. The ^{1}H-NMR spectra were determined with a Hitachi R-600 spectrometer (60 MHz) in deuteriochloroform with tetramethylsilane used as an internal standard; the chemical shifts are expressed in δ values. The IR and UV spectra were taken with a JASCO FT/IR-5300 infrared and Hitachi 220 spectrophotometers, respectively.

Preparation of 3-(Mercaptomethylene)-2(3*H*)-indolizinone Derivatives These (*Z*)-3-[mercapto(methylthio)- **3a**—**d** and (*Z*)-3-[mercapto(phenacylthio)methylene]-2(3*H*)-indolizinone derivatives **3e**—**p** were prepared from the alkaline treatment of 1-ethoxycarbonylmethyl-2-ethyl, 2-propyl-, 2-benzyl-, and 2-(*p*-chlorobenzyl)pyridinium bromides (**1a**—**d**) followed by the reactions of the resulting 2(3*H*)-indolizinones with carbon disulfide and dimethyl sulfate (**2a**) or phenacyl bromides (**2b**—**d**) in the presence of alkali, according to the procedure reported earlier by us.[2a)]

Some data for new compounds **3a**, **b**, **d**—**p** are as follows:

(*Z*)-3-[Mercapto(methylthio)methylene]-1-methyl-2(3*H*)-indolizinone (**3a**): 65% (from **1a**, CS_2, and **2a**), orange needles, mp 134—135 °C, IR (KBr) 1588 cm^{-1} (CO), 2580 cm^{-1} (SH), NMR ($CDCl_3$) 2.01 (3H, s, 1-CH_3), 2.87 (3H, s, SCH_3), 6.78 (1H, m, 6-H), 6.9—7.5 (2H, m, 7-, 8-H), 9.38 (1H, br d, *J*=7.0 Hz, 5-H), 12.86 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 246 (6190), 283 (6340), 321 (10070), 387 (11550), 451 (12730). *Anal.* Calcd for $C_{11}H_{11}NOS_2$: C, 55.67; H, 4.67; N, 5.90. Found: C, 55.85; H, 4.62; N, 5.76.

1-Ethyl-(*Z*)-3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinone (**3b**): 30% (from **1b**, CS_2, and **2a**), orange needles, mp 78—80 °C, IR (KBr) 1585 cm^{-1} (CO), 2580 cm^{-1} (SH), NMR ($CDCl_3$) 1.20 (3H, t, *J*=7.0 Hz, 1-$CH_2\underline{CH_3}$), 2.66 (2H, q, *J*=7.0 Hz, 1-$C\underline{H_2}CH_3$), 2.83 (3H, s, SCH_3), 6.66 (1H, m, 6-H), 6.9—7.4 (2H, m, 7-, 8-H), 9.33 (1H, br d, *J*=7.0 Hz, 5-H), 12.50 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 245 (8910), 283 (8260), 322 (11840), 385 (13700), 452 (14210). *Anal.* Calcd for $C_{12}H_{13}NOS_2$: C, 57.34; H, 5.21; N, 5.57. Found: C, 57.20; H, 5.31; N, 5.31.

1-(*p*-Chlorophenyl)-(*Z*)-3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinone (**3d**): 65% (from **1d**, CS_2, and **2a**), orange needles, mp 153—154 °C, IR (KBr) 1585 cm^{-1} (CO), 2520 cm^{-1} (SH), NMR ($CDCl_3$) 2.82 (3H, s, SCH_3), 6.84 (1H, dt, *J*=7.0, 7.0, 2.0 Hz, 6-H), 7.1—7.8 (6H, m, phenyl-, 7-, 8-H), 9.54 (1H, br d, *J*=7.0 Hz, 5-H), 13.22 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 253 (6370), 302 (13540), 402 (11470), 453 (7450). *Anal.* Calcd for $C_{16}H_{12}ClNOS_2$: C, 57.56; H, 3.62; N, 4.20. Found: C, 57.53; H, 3.81; N, 4.04.

(*Z*)-3-[Mercapto(phenacylthio)methylene]-1-methyl-2(3*H*)-indolizinone (**3e**): 50% (from **1a**, CS_2, **2b**), orange needles, mp 184—186 °C, IR (KBr) 1589, 1685 cm^{-1} (CO), 2633 cm^{-1} (SH), NMR ($CDCl_3$) 2.18 (3H, s, 1-CH_3), 5.14 (2H, s, SCH_2CO), 6.90 (1H, m, 6-H), 7.3—8.3 (7H, m, phenyl-, 7-, 8-H), 9.64 (1H, br d, *J*=7.0 Hz, 5-H), 12.30 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 242 (20170), 322 (12170), 390 (14040), 399 (14040), 450 (12090). *Anal.* Calcd for $C_{18}H_{15}NO_2S_2$: C, 63.32; H, 4.43; N, 4.10. Found: C, 63.42; H, 4.41; N, 4.02.

1-Ethyl-(*Z*)-3-[mercapto(phenacylthio)methylene]-2(3*H*)-indolizinone (**3f**): 63% (from **1b**, CS_2, **2b**), orange prisms, mp 140—142 °C, IR (KBr) 1589, 1689 cm^{-1} (CO), 2619 cm^{-1} (SH), NMR ($CDCl_3$) 1.23 (3H, t, *J*=7.0 Hz, 1-$CH_2\underline{CH_3}$), 2.72 (2H, q, *J*=7.0 Hz, 1-$C\underline{H_2}CH_3$), 5.13 (2H, s, SCH_2CO), 6.88 (1H, m, 6-H), 7.3—8.3 (7H, m, phenyl-, 7-, 8-H), 9.59 (1H, br d, *J*=7.0 Hz, 5-H), 12.34 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 242 (8790), 283 (5010), 321 (6110), 391 (7490), 399 (7390), 452 (6530). *Anal.* Calcd for $C_{19}H_{17}NO_2S_2$: C, 64.20; H, 4.82; N, 3.94. Found: C, 64.47; H, 4.71; N, 3.78.

(*Z*)-3-[Mercapto(methylthio)methylene]-1-phenyl-2(3*H*)-indolizinone (**3g**): 40% (from **1c**, CS_2, **2b**), orange needles, mp 141—143 °C, IR (KBr) 1583, 1682 cm^{-1} (CO), 2567 cm^{-1} (SH), NMR ($CDCl_3$) 5.12 (2H, s, SCH_2CO), 6.95 (1H, dt, *J*=7.0, 7.0, 2.0 Hz, 6-H), 7.2—8.4 (12H, m, phenyl-, 7-, 8-H), 9.68 (1H, br d, *J*=7.0 Hz, 5-H), 12.64 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 240 (17740), 294 (16330), 405 (17760), 450 (5560). *Anal.* Calcd for $C_{23}H_{17}NO_2S_2$: C, 68.46; H, 4.25; N, 3.47. Found: C, 68.54; H, 4.22; N, 3.42.

1-(*p*-Chlorophenyl)-(*Z*)-3-[mercapto(methylthio)methylene]-2(3*H*)-indolizinone (**3h**): 32% (from **1d**, CS_2, **2b**), orange prisms, mp 170—172 °C, IR (KBr) 1595, 1676 cm^{-1} (CO), 2463 cm^{-1} (SH), NMR ($CDCl_3$) 5.16 (2H, s, SCH_2CO), 7.00 (1H, m, 6-H), 7.3—8.3 (11H, m, phenyl-, 7-, 8-H), 9.70 (1H, br d, *J*=7.0 Hz, 5-H), 12.66 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 241 (18410), 301 (21080), 404 (22040), 456 (7350). *Anal.* Calcd for $C_{23}H_{16}ClNO_2S_2$: C, 63.08; H, 3.68; N, 3.20. Found: C, 63.11; H, 3.65; N, 3.20.

(*Z*)-3-[(*p*-Chlorophenacylthio)mercaptomethylene]-1-methyl-2(3*H*)-indolizinone (**3i**): 55% (from **1a**, CS_2, **2c**), orange prisms, mp 200—202 °C, IR (KBr) 1587, 1693 cm^{-1} (CO), 2609 cm^{-1} (SH), NMR ($CDCl_3$) 2.18 (3H, s, 1-CH_3), 5.06 (2H, s, SCH_2CO), 6.96 (1H, m, 6-H), 7.3—8.3 (6H, m, phenyl-, 7-, 8-H), 9.54 (1H, br d, *J*=7.0 Hz, 5-H), 12.28 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 254 (20090), 322 (10790), 404 (13430), 450 (11250). *Anal.* Calcd for $C_{18}H_{14}ClNO_2S_2$: C, 57.52; H, 3.75; N, 3.73. Found: C, 57.38; H, 3.69; N, 3.65.

(*Z*)-3-[(*p*-Chlorophenacylthio)mercaptomethylene]-1-ethyl-2(3*H*)-indolizinone (**3j**): 62% (from **1b**, CS_2, **2c**), orange prisms, mp 173—175 °C, IR (KBr) 1589, 1697 cm^{-1} (CO), 2611 cm^{-1} (SH), NMR ($CDCl_3$) 1.24 (3H, t, *J*=7.0 Hz, 1-$CH_2\underline{CH_3}$), 2.72 (2H, q, *J*=7.0 Hz, 1-$C\underline{H_2}CH_3$), 5.10 (2H, s, SCH_2CO), 6.98 (1H, m, 6-H), 7.4—8.3 (6H, m, phenyl-, 7-, 8-H), 9.60 (1H, br d, *J*=7.0 Hz, 5-H), 12.36 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 253 (19920), 320 (11760), 402 (14100), 451 (12140). *Anal.* Calcd for $C_{19}H_{16}ClNO_2S_2$: C, 58.53; H, 4.14; N, 3.59. Found: C, 58.61; H, 4.11; N, 3.54.

(*Z*)-3-[(*p*-Chlorophenacylthio)mercaptomethylene]-1-phenyl-2(3*H*)-indolizinone (**3k**): 47% (from **1c**, CS_2, **2c**), orange needles, mp 177—179 °C, IR (KBr) 1581, 1684 cm^{-1} (CO), 2590 cm^{-1} (SH), NMR ($CDCl_3$) 5.10 (2H, s, SCH_2CO), 7.00 (1H, dt, *J*=7.0, 7.0, 2.0 Hz, 6-H), 7.3—8.2 (11H, m, phenyl-, 7-, 8-H), 9.71 (1H, br d, *J*=7.0 Hz, 5-H), 12.70 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 251 (27590), 294 (21870), 406 (22080), 452 (9420). *Anal.* Calcd for $C_{23}H_{16}ClNO_2S_2$: C, 63.08; H, 3.68; N, 3.20. Found: C, 63.27; H, 3.59; N, 3.10.

1-(*p*-Chlorophenyl)-(*Z*)-3-[(*p*-chlorophenacylthio)mercaptomethylene]-2(3*H*)-indolizinone (**3l**): 45% (from **1d**, CS_2, **2c**), orange prisms, mp 194—196 °C, IR (KBr) 1583, 1682 cm^{-1} (CO), 2555 cm^{-1} (SH), NMR ($CDCl_3$) 5.06 (2H, s, SCH_2CO), 6.98 (1H, m, 6-H), 7.3—8.3 (10H, m, phenyl-, 7-, 8-H), 9.66 (1H, br d, *J*=7.0 Hz, 5-H), 12.58 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 251 (15360), 297 (14370), 405 (15320), 452 (2570). *Anal.* Calcd for $C_{23}H_{15}Cl_2NO_2S_2$: C, 58.48; H, 3.20; N, 2.96. Found: C, 58.37; H, 3.39; N, 2.88.

(*Z*)-3-[(*p*-Bromophenacylthio)mercaptomethylene]-1-methyl-2(3*H*)-indolizinone (**3m**): 46% (from **1a**, CS_2, **2d**), orange prisms, mp 199—201 °C, IR (KBr) 1593, 1697 cm^{-1} (CO), 2592 cm^{-1} (SH), NMR ($CDCl_3$) 2.06 (3H, s, 1-CH_3), 4.96 (2H, s, SCH_2CO), 6.86(1H, m, 6-H), 7.2—8.1 (6H, m, aromatic, 7-, 8-H), 9.48 (1H, br d, *J*=7.0 Hz, 5-H), 12.22 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 257 (22210), 321 (12040), 402 (13480), 451 (11490). *Anal.* Calcd for $C_{18}H_{14}BrNO_2S_2$: C, 51.43; H, 3.36; N, 3.33. Found: C, 51.21; H, 3.30; N, 3.29.

(*Z*)-3-[(*p*-Bromophenacylthio)mercaptomethylene]-1-ethyl-2(3*H*)-indolizinone (**3n**): 76% (from **1b**, CS_2, **2d**), orange prisms, mp 174—176 °C, IR (KBr) 1589, 1697 cm^{-1} (CO), 2611 cm^{-1} (SH), NMR ($CDCl_3$) 1.22 (3H, t, *J*=7.0 Hz, 1-$CH_2\underline{CH_3}$), 2.70 (2H, q, *J*=7.0 Hz, 1-$C\underline{H_2}CH_3$), 5.04 (2H, s, SCH_2CO), 6.92 (1H, m, 6-H), 7.3—8.2 (6H, m, phenyl-, 7-, 8-H), 9.54 (1H, br d, *J*=7.0 Hz, 5-H), 12.30 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 255 (16840), 322 (8100), 402 (9490), 453 (7330). *Anal.* Calcd for $C_{19}H_{16}BrNO_2S_2$: C, 52.54; H, 3.71; N, 3.22. Found: C, 52.63; H, 3.77; N, 3.07.

(Z)-3-[(*p*-Bromophenacylthio)mercaptomethylene]-1-phenyl-2(3*H*)-indolizinone (**3o**): 50% (from **1c**, CS_2, **2d**), orange needles, mp 181—183 °C, IR (KBr) 1581, 1670 cm^{-1} (CO), 2565 cm^{-1} (SH), NMR ($CDCl_3$) 5.04 (2H, s, SCH_2CO), 6.96 (1H, dt, *J*=7.0, 7.0, 2.0 Hz, 6-H), 7.2—8.2 (11H, m, phenyl-, 7-, 8-H), 9.64 (1H, br d, *J*=7.0 Hz, 5-H), 12.58 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 254 (21350), 294 (16520), 405 (17250), 449 (6450). *Anal.* Calcd for $C_{23}H_{16}BrNO_2S_2$: C, 57.26; H, 3.34; N, 2.90. Found: C, 57.38; H, 3.33; N, 2.79.

(*Z*)-3-[(*p*-Bromophenacylthio)mercaptomethylene]-1-(*p*-chlorophenyl)-2(3*H*)-indolizinone (**3p**): 60% (from **1d**, CS_2, **2d**), orange prisms, mp 185—187 °C, IR (KBr) 1581, 1678 cm^{-1} (CO), 2633 cm^{-1} (SH), NMR ($CDCl_3$) 5.06 (2H, s, SCH_2CO), 6.98 (1H, m, 6-H), 7.3—8.2 (10H, m, phenyl-, 7-, 8-H), 9.62 (1H, br d, *J*=7.0 Hz, 5-H), 12.60 (1H, s, SH). UV λ_{max} (EtOH) nm (ε): 253 (20240), 297 (19250), 405 (20930), 451 (3830). *Anal.* Calcd for $C_{23}H_{15}BrClNO_2S_2$: C, 53.45; H, 2.93; N, 2.71. Found: C, 53.60; H, 2.83; N, 2.66.

Reactions of 3-(Mercaptomethylene)-2(3*H*)-indolizinones with Various Alkyl Halides. General Method A chloroform solution (30 ml) of 3-

(mercaptomethylene)-2(3*H*)-indolizinone (**3**, 1 mmol) and an alkylating agent (**2** or **4**, 1.2 mmol)[6] was treated with DBU (1.2 mmol) at room temperature for 12 h. The resulting mixture was concentrated at reduced pressure and the residue was separated by column chromatography on alumina using chloroform as an eluent. The red chloroform layers involving the product were combined and concentrated at reduced pressure. The crude product was recrystallized from chloroform–hexane to provide the corresponding 4(1*H*)-8,8a-dihydro-1,4-thiazino[3,4,5-*cd*]indolizinone derivatives or (*E*)-3-(5-aryl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinones.

In the reactions of **3a**, **c** with bromoacetonitrile (**4a**) no significant products could be isolated.

Some data for these products **5b**, **d**—**i** and **6a**—**l** are as follows:

3-Methylthio-4-oxo-5-phenyl-(1*H*)-8,8a-dihydro-1,4-thiazino[3,4,5-*cd*]indolizine-1-carbonitrile (**5b**): 13% (from **3c** and **4a**), red prisms, mp 190—192 °C, IR (KBr) 1618 cm^{-1} (CO), 2239 cm^{-1} (CN), NMR ($CDCl_3$) 2.52 (3H, s, SCH_3), 2.2—3.0 (2H, m, 8-H), 4.09 (1H, d, J=2.0 Hz, 1H), 4.20 (1H, m, 8a-H), 6.25 (1H, m, 7-H), 6.72 (1H, dd, J=10.0, 2.5 Hz, 6-H), and 7.0—7.7 (5H, m, phenyl-H). UV λ_{max} (EtOH) nm (ε): 251 (21910), 292 (6350), 370 (12650), 486 (6790). *Anal.* Calcd for $C_{18}H_{14}N_2OS_2$: C, 63.88; H, 4.17; N, 8.28. Found: C, 63.92; H, 4.29; N, 8.12.

Ethyl 5-Methyl-3-methylthio-4-oxo-(1*H*)-8,8a-dihydro-1,4-thiazino-[3,4,5-*cd*]indolizine-1-carboxylate (**5d**): 22% (from **3a** and **4b**), red prisms, mp 106—109 °C, IR (KBr) 1714, 1610 cm^{-1} (CO), NMR ($CDCl_3$) 1.35 (3H, t, J=7.0 Hz, $OCH_2C\underline{H}_3$), 1.80 (3H, s, 5-CH_3), 2.53 (3H, s, SCH_3), 2.2—3.1 (2H, m, 8-H), 4.0—4.7 (4H, m, 1-, 8a-H, $OC\underline{H}_2CH_3$), 6.19 (1H, m, 7-H), 6.49 (1H, dd, J=10.0, 2.5 Hz, 6-H). UV λ_{max} (EtOH) nm (ε): 237 (14260), 290 (3350), 368 (11920), 475 (4940). *Anal.* Calcd for $C_{15}H_{17}NO_3S_2$: C, 55.70; H, 5.30; N, 4.33. Found: C, 55.61; H, 5.13; N, 4.20.

Ethyl 3-Methylthio-4-oxo-5-phenyl-(1*H*)-8,8a-dihydro-1,4-thiazino[3,4,5-*cd*]indolizine-1-carboxylate (**5e**): 36% (from **3c** and **4b**), red needles, mp 151—152 °C, IR (KBr) 1720, 1612 cm^{-1} (CO), NMR ($CDCl_3$) 1.32 (3H, t, J=7.0 Hz, $OCH_2C\underline{H}_3$), 2.53 (3H, s, SCH_3), 2.2—2.8 (2H, m, 8-H), 4.0—4.7 (4H, m, 1-, 8a-H, $OC\underline{H}_2CH_3$), 6.25 (1H, m, 7-H), 6.68 (1H, dd, J=10.0, 2.5 Hz, 6-H), and 7.1—7.7 (5H, m, phenyl-H). UV λ_{max} (EtOH) nm (ε): 250 (19270), 292 (10600), 373 (9950), 477 (5240), 487 (5130). *Anal.* Calcd for $C_{20}H_{19}NO_3S_2$: C, 62.31; H, 4.97; N, 3.63. Found: C, 62.48; H, 4.68; N, 3.85.

Ethyl 5-(*p*-Chlorophenyl)-3-methylthio-4-oxo -(1*H*)-8,8a-dihydro-1,4-thiazino[3,4,5-*cd*]indolizine-1-carboxylate (**5f**): 42% (from **3d** and **4b**), red prisms, mp 158—160 °C, IR (KBr) 1726, 1615 cm^{-1} (CO), NMR ($CDCl_3$) 1.33 (3H, t, J=7.0 Hz, $OCH_2C\underline{H}_3$), 2.50 (3H, s, SCH_3), 2.2—2.9 (2H, m, 8-H), 4.0—4.7 (4H, m, 1-, 8a-H, $OC\underline{H}_2CH_3$), 6.25 (1H, m, 7-H), 6.63 (1H, dd, J=10.0, 2.5 Hz, 6-H), 7.0—7.7 (4H, m, phenyl-H). UV λ_{max} (EtOH) nm (ε): 258 (17130), 293 (8010), 376 (9290), 481 (4980), 487 (4990). *Anal.* Calcd for $C_{20}H_{18}ClNO_3S_2$: C, 57.20; H, 4.32; N, 3.34. Found: C, 57.18; H, 4.44; N, 3.24.

tert-Butyl 5-Methyl-3-methylthio-4-oxo-(1*H*)-8,8a-dihydro-1,4-thiazino-[3,4,5-*cd*]indolizine-1-carboxylate (**5g**): 31% (from **3a** and **4c**), orange prisms, mp 165—166 °C, IR (KBr) 1724, 1614 cm^{-1} (CO), NMR ($CDCl_3$) 1.54 (9H, s, *tert*-Bu), 1.80 (3H, s, 5-CH_3), 2.52 (3H, s, SCH_3), 2.1—3.2 (2H, m, 8-H), 4.02 (1H, d, J=2.0 Hz, 1-H), 4.02 (1H, m, 8a-H), 6.10 (1H, m, 7-H), 6.41 (1H, dd, J=10.0, 2.5 Hz, 6-H). UV λ_{max} (EtOH) nm (ε): 237 (13910), 292 (3980), 369 (12250), 473 (5170). *Anal.* Calcd for $C_{17}H_{21}NO_3S_2$: C, 58.09; H, 6.02; N, 3.99. Found: C, 58.20; H, 5.98; N, 3.92.

tert-Butyl 3-Methylthio-4-oxo-5-phenyl-(1*H*)-8,8a-dihydro-1,4-thiazino-[3,4,5-*cd*]indolizine-1-carboxylate (**5h**): 37% (from **3c** and **4c**), red needles, mp 151—152 °C, IR (KBr) 1723, 1616 cm^{-1} (CO), NMR ($CDCl_3$) 1.52 (9H, s, *tert*-Bu), 2.51 (3H, s, SCH_3), 2.2—3.2 (2H, m, 8-H), 4.11 (1H, d, J=2.0 Hz, 1-H), 4.16 (1H, m, 8a-H), 6.22 (1H, m, 7-H), 6.66 (1H, dd, J=10.0, 2.5 Hz, 6-H), 7.0—7.7 (5H, m, phenyl-H). UV λ_{max} (EtOH) nm (ε): 252 (28830), 290 (9800), 379 (14200), 484 (9010). *Anal.* Calcd for $C_{22}H_{23}NO_3S_2$: C, 63.89; H, 5.61; N, 3.39. Found: C, 63.77; H, 5.73; N, 3.10.

tert-Butyl 5-(*p*-Chlorophenyl)-3-methylthio-4-oxo-(1*H*)-8,8a-dihydro-1,4-thiazino[3,4,5-*cd*]indolizine-1-carboxylate (**5i**): 43% (from **3d** and **4c**), red needles, mp 181—183 °C, IR (KBr) 1727, 1625 cm^{-1} (CO), NMR ($CDCl_3$) 1.54 (9H, s, *tert*-Bu), 2.53 (3H, s, SCH_3), 2.2—3.2 (2H, m, 8-H), 4.10 (1H, d, J=2.0 Hz, 1-H), 4.16 (1H, m, 8a-H), 6.22 (1H, m, 7-H), 6.59 (1H, dd, J=10.0, 2.5 Hz, 6-H), 7.1—7.6 (4H, m, phenyl-H). UV λ_{max} (EtOH) nm (ε): 258 (25330), 291 (13650), 382 (14150), 482 (8790). *Anal.* Calcd for $C_{22}H_{22}ClNO_3S_2$: C, 58.98; H, 4.95; N, 3.13. Found: C, 59.05; H, 5.25; N, 2.88.

1-Methyl-(*E*)-3-(5-phenyl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinone (**6a**): 43% (from **3a** and **2b**) or 33% (from **3e** and **2e**), red prisms, mp 254—256 °C, IR (KBr) 1649 cm^{-1} (CO), NMR ($CDCl_3$) 1.91 (3H, s, 1-CH_3), 6.35 (1H, m, 6-H), 6.86 (1H, s, 4′-H), 7.0—7.7 (7H, m, 7-, 8-H, phenyl-H), 8.49 (1H, d, J=7.0 Hz, 5-H). UV λ_{max} (EtOH) nm (ε): 230 (18480), 249 (17250), 318 (12690), 402 (26210), 505 (2360). *Anal.* Calcd for $C_{18}H_{13}NO_2S$: C, 70.34; H, 4.26; N, 4.56. Found: C, 70.33; H, 4.22; N, 4.61.

(*E*)-3-[5-(*p*-Chlorophenyl-1,3-oxathiol-2-ylidene]-1-methyl-2(3*H*)-indolizinone (**6b**): 38% (from **3a** and **2c**) or 50% (from **3i** and **2e**), red prisms, mp 253—255 °C, IR (KBr) 1639 cm^{-1} (CO), NMR ($CDCl_3$) 1.99 (3H, s, 1-CH_3), 6.39 (1H, m, 6-H), 6.91 (1H, s, 4′-H), 7.0—7.8 (6H, m, 7-, 8-H, phenyl-H), 8.34 (1H, d, J=7.0 Hz, 5-H). UV λ_{max} (EtOH) nm (ε): 248 (23420), 319 (13020), 402 (24550), 505 (1420). *Anal.* Calcd for $C_{18}H_{12}ClNO_2S$: C, 63.25; H, 3.54; N, 4.10. Found: C, 63.37; H, 3.52; N, 3.99.

(*E*)-3-[5-(*p*-Bromophenyl-1,3-oxathiol-2-ylidene]-1-methyl-2(3*H*)-indolizinone (**6c**): 46% (from **3a** and **2d**) or 23% (from **3m** and **2e**), red prisms, mp 260—262 °C, IR (KBr) 1639 cm^{-1} (CO), NMR ($CDCl_3$) 1.98 (3H, s, 1-CH_3), 6.34 (1H, m, 6-H), 6.92 (1H, s, 4′-H), 7.0—7.8 (6H, m, 7-, 8-H, phenyl-H), 8.32 (1H, d, J=7.0 Hz, 5-H). UV λ_{max} (EtOH) nm (ε): 250 (25970), 320 (14190), 401 (25550), 503 (2400). *Anal.* Calcd for $C_{18}H_{12}BrNO_2S$: C, 53.48; H, 3.49; N, 3.46. Found: C, 53.56; H, 3.43; N, 3.43.

1-Ethyl-(*E*)-3-(5-phenyl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinone (**6d**): 32% (from **3b** and **2b**) or 29% (from **3f** and **2e**), red prisms, mp 225—227 °C, IR (KBr) 1639 cm^{-1} (CO), NMR ($CDCl_3$) 1.19 (3H, t, J=7.0 Hz, 1-$CH_2C\underline{H}_3$), 2.53 (2H, q, J=7.0 Hz, 1-$C\underline{H}_2CH_3$), 6.39 (1H, m, 6-H), 6.90 (1H, s, 4′-H), 7.0—7.8 (7H, m, 7-, 8-H, phenyl-H), 8.36 (1H, d, J=7.0 Hz, 5-H). UV λ_{max} (EtOH) nm (ε): 231 (19870), 248 (17960), 318 (12690), 401 (25850), 500 (1810). *Anal.* Calcd for $C_{19}H_{15}NO_2S+H_2O$: C, 67.24; H, 5.05; N, 4.13. Found: C, 66.95; H, 4.96; N, 4.04.

(*E*)-3-[5-(*p*-Chlorophenyl-1,3-oxathiol-2-ylidene]-1-ethyl-2(3*H*)-indolizinone (**6e**): 17% (from **3b** and **2c**) or 31% (from **3j** and **2e**), red prisms, mp 239—241 °C, IR (KBr) 1647 cm^{-1} (CO), NMR ($CDCl_3$) 1.19 (3H, t, J=7.0 Hz, 1-$CH_2C\underline{H}_3$), 2.53 (2H, q, J=7.0 Hz, 1-$C\underline{H}_2CH_3$), 6.45 (1H, m, 6-H), 6.90 (1H, s, 4′-H), 7.0—7.9 (6H, m, 7-, 8-H, phenyl-H), 8.49 (1H, d, J=7.0 Hz, 5-H). UV λ_{max} (EtOH) nm (ε): 248 (23690), 319 (13720), 401 (24970), 507 (2350). *Anal.* Calcd for $C_{19}H_{14}ClNO_2S$: C, 64.13; H, 3.97; N, 3.94. Found: C, 63.83; H, 4.06; N, 4.15.

(*E*)-3-[5-(*p*-Bromophenyl-1,3-oxathiol-2-ylidene]-1-ethyl-2(3*H*)-indolizinone (**6f**): 12% (from **3b** and **2d**) or 50% (from **3n** and **2e**), red prisms, mp 229—231 °C, IR (KBr) 1651 cm^{-1} (CO), NMR ($CDCl_3$) 1.18 (3H, t, J=7.0 Hz, 1-$CH_2C\underline{H}_3$), 2.52 (2H, q, J=7.0 Hz, 1-$C\underline{H}_2CH_3$), 6.38 (1H, m, 6-H), 6.91 (1H, s, 4′-H), 7.0—7.9 (6H, m, 7-, 8-H, phenyl-H), 8.34 (1H, d, J=7.0 Hz, 5-H). UV λ_{max} (EtOH) nm (ε): 250 (29990), 321 (15180), 401 (28100), 507 (830). *Anal.* Calcd for $C_{19}H_{14}BrNO_2S+H_2O$: C, 54.56; H, 3.86; N, 3.35. Found: C, 54.61; H, 3.89; N, 3.27.

1-Phenyl-(*E*)-3-(5-phenyl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinone (**6g**): 74% (from **3c** and **2b**) or 48% (from **3g** and **2e**), red prisms, mp 250—251 °C, IR (KBr) 1653 cm^{-1} (CO), NMR ($CDCl_3$) 6.53 (1H, dt, J=7.0, 7.0, 2.0 Hz, 6-H), 6.91 (1H, s, 4′-H), 7.0—8.0 (12H, m, 7-, 8-H, phenyl-H), 8.56 (1H, d, J=7.0 Hz, 5-H). UV λ_{max} (EtOH) nm (ε): 228 (22460), 298 (20430), 405 (25740), 507 (2330). *Anal.* Calcd for $C_{23}H_{15}NO_2S$: C, 74.48; H, 4.26; N, 3.12. Found: C, 74.66; H, 3.99; N, 3.73.

(*E*)-3-[5-(*p*-Chlorophenyl-1,3-oxathiol-2-ylidene]-1-phenyl-2(3*H*)-indolizinone (**6h**): 65% (from **3c** and **2c**) or 53% (from **3k** and **2e**), red prisms, mp 270—272 °C, IR (KBr) 1647 cm^{-1} (CO), NMR ($CDCl_3$) 6.57 (1H, dt, J=7.0, 7.0, 2.0 Hz, 6-H), 6.90 (1H, s, 4′-H), 7.0—8.0 (11H, m, 7-, 8-H, phenyl-H), 8.46 (1H, d, J=7.0 Hz, 5-H). UV λ_{max} (EtOH) nm (ε): 232 (21260), 246 (22140), 300 (20630), 403 (27630), 506 (2020). *Anal.* Calcd for $C_{23}H_{14}ClNO_2S$: C, 68.40; H, 3.49; N, 3.47. Found: C, 68.51; H, 3.43; N, 3.41.

(*E*)-3-[5-(*p*-Bromophenyl)-1,3-oxathiol-2-ylidene)-1-phenyl-2(3*H*)-indolizinone (**6i**): 68% (from **3c** and **2d**) or 38% (from **3o** and **2e**), red prisms, mp 272—275 °C, IR (KBr) 1645 cm^{-1} (CO), NMR ($CDCl_3$) 6.56 (1H, m, 6-H), 6.96 (1H, s, 4′-H), 7.0—8.0 (11H, m, 7-, 8-H, phenyl-H), 8.52 (1H, d, J=7.0 Hz, 5-H). UV λ_{max} (EtOH) nm (ε): 232 (21860), 248 (24160), 301 (22050), 404 (29430), 506 (1630). *Anal.* Calcd for $C_{23}H_{14}BrNO_2S$: C, 61.62; H, 3.15; N, 3.12. Found: C, 61.43; H, 3.07; N, 3.07.

1-(*p*-Chlorophenyl)-(*E*)-3-(5-phenyl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinone (**6j**): 19% (from **3d** and **2b**) or 27% (from **3h** and **2e**), purple prisms, mp 274—276 °C, IR (KBr) 1653 cm^{-1} (CO), NMR ($CDCl_3$) 6.61 (1H, m, 6-H), 6.94 (1H, s, 4′-H), 7.0—7.9 (11H, m, 7-, 8-H, phenyl-H), 8.58 (1H, d, J=7.0 Hz, 5-H). UV λ_{max} (EtOH) nm (ε): 227 (21170), 309 (21630), 405 (26180), 507 (820). *Anal.* Calcd for $C_{23}H_{14}ClNO_2S$: C, 68.40; H, 3.49; N, 3.47. Found: C, 68.54; H, 3.48; N, 3.44.

1-(*p*-Chlorophenyl)-(*E*)-3-[5-(*p*-chlorophenyl-1,3-oxathiol-2-ylidene]-2(3*H*)-indolizinone (**6k**): 34% (from **3d** and **2c**) or 22% (from **3l** and **2e**),

purple prisms, mp 282—284 °C, IR (KBr) 1653 cm^{-1} (CO), NMR ($CDCl_3$) 6.59 (1H, m, 6-H), 6.95 (1H, s, 4′-H), 7.0—7.8 (10H, m, 7-, 8-H, phenyl-H), 8.53 (1H, d, J=7.0 Hz, 5-H). UV λ_{max} (EtOH) nm (ε): 233 (19150), 244 (18650), 309 (20850), 404 (23580), 504 (1230). *Anal.* Calcd for $C_{23}H_{13}Cl_2NO_2S$: C, 63.02; H, 2.99; N, 3.20. Found: C, 62.83; H, 2.97; N, 3.15.

(*E*)-3-[5-(*p*-Bromophenyl-1,3-oxathiol-2-ylidene]-1-(*p*-chlorophenyl)-2(3*H*)-indolizinone (**6l**): 28% (from **3d** and **2d**) or 35% (from **3p** and **2e**), purple prisms, mp 278—280 °C, IR (KBr) 1647 cm^{-1} (CO), NMR ($CDCl_3$) 6.64 (1H, m, 6-H), 6.93 (1H, s, 4′-H), 7.0—7.9 (10H, 7-, 8-H, phenyl-H), 8.51 (1H, d, J=7.0 Hz, 5-H). UV λ_{max} (EtOH) nm (ε): 234 (20820), 248 (22340), 310 (23560), 404 (28000), 502 (2280). *Anal.* Calcd for $C_{23}H_{12}BrClNO_2S+2H_2O$: C, 53.25; H, 3.30; N, 2.70. Found: C, 53.52; H, 3.15; N, 2.58.

Crystallography of 1-Phenyl-(*E*)-3-(5-phenyl-1,3-oxathiol-2-ylidene)-2(3*H*)-indolizinone (6g) A single crystal (0.06×0.42×0.68 mm) grown from $CHCl_3$–hexane was used for the unit-cell determinations and the data collections of a Rigaku AFC5S four-circle diffractometer, with graphite-monochromated MoK_α radiation (λ=0.71069 Å). Crystal data of **6g**: $C_{23}H_{15}NO_2S$; M=369.44; orthorhombic, space group *Pbca* (#61), Z=8 with a=18.662 (5) Å, b=19.454 (11) Å, c=9.701 (3) Å; V=3522 (2) $Å^3$, and $D_{calc.}$=1.393 g/cm^3. All calculations were performed using the TEXSAN program.[7] The structure was solved by a direct method (MITHRIL).[8] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically. The final R- and R_w-factors after full-matrix least-squares refinements were 0.059 and 0.057 for 1877 ($I>2.00\sigma(I)$) respectively observed reflections.

References and Notes

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3) UV spectra of **3c**: λ_{max} (EtOH) nm (ε): 250 (10480), 296 (11710), 319 (122500), 386 (11850), 455 (9230).
4) This red shift may be due to the loss of potencial aromaticity of 3-methylene-2(3*H*)-indolizinone skeleton.
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7) "TEXSAN TEXRAY," Structure Analysis Package, Molecular Structure Corporation (1985).
8) Gilmore C. J., *J. Appl. Cryst.*, **17**, 42—46 (1984).