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PREPARATION OF NEW NITROGEN-BRIDGED HETEROCYCLES. 63.[1] UNEXPECTED FORMATION OF THIENO[3',4':4,5]IMIDAZO[1,2-*a*]-PYRIDINES")

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Abstract – The alkaline treatment and dehydrogenation of pyridinium salts, obtainable from the *S*-alkylation of 3,5-dimethylpyridinium 2-alkylthio-1-cyano-2-thioxoethylides with some phenacyl bromides, afforded unexpected heterocycles, 3-alkylthio-1-arylcarbonyl-6,8-dimethylthieno[3',4':4,5]imidazo-[1,2-*a*]pyridines, together with the corresponding 2-alkylthio-1-arylcarbonylthio-6,8-dimethyl-indolizine-3-carbonitriles. **(MS Word Style "04 Het-Abstract")**

Recently we reported a first ring contraction-desulfurization route of transient 1-(arylcarbonyl)-7,9-dimethylpyrido[1,2-*d*]-1,4-thiazines having a 4-ethoxycarbonyl group and the smooth transformation from the resulting ethyl 1-arylcarbonyl-6,8-dimethyl-2-(*R*-thio)indolizine-3-carboxylates to ethyl 3-aryl-4,6-dimethylthieno[3,2-*a*]indolizine-9-carboxylates.[2] In expectation of this ring contraction-desulfurization type of reaction, we next examined the reactions of pyridinium salts which were obtained from 3,5-dimethylpyridinium 2-alkylthio-1-cyano-2-thioxoethylides[3] and some phenacyl bromides. However, the initially expected products, 1-arylcarbonyl-6,8-dimethylindolizine-3-carbonitriles, were not formed at all. Instead, we found the formation of another type of heterocycle, thieno[3',4':4,5]-

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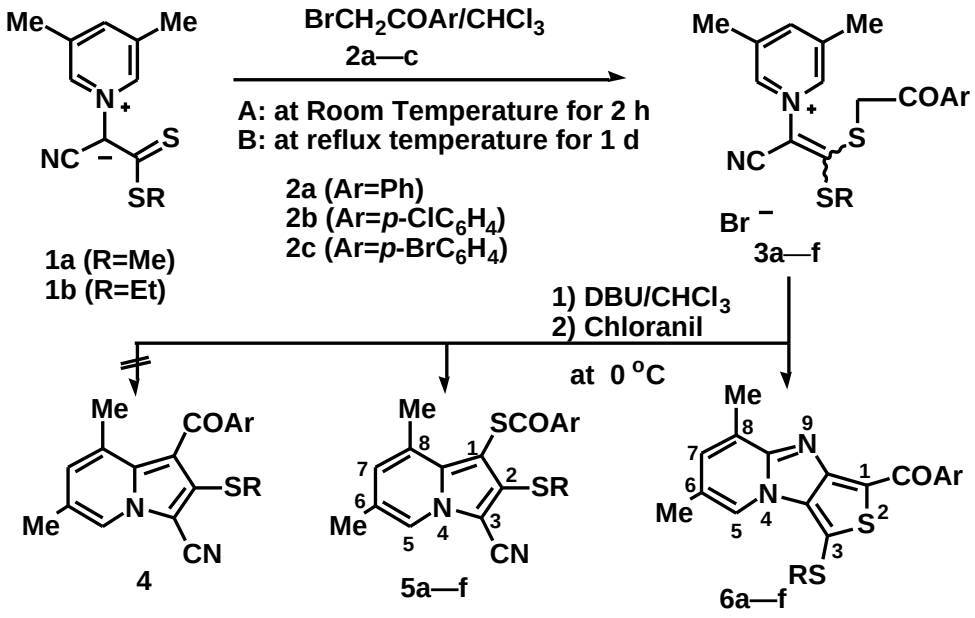
Dedicated to Prof. Dr. Ryoji Noyori on the occasion of his 70th birthday.

imidazo[1,2-*a*]pyridines, together with the ring contraction-rearrangement products,[4] 1-(arylcarbonylthio)indolizine-3-carbonitiriles, as major products. In this paper we report the unexpected formation of the title compounds in the reaction of the 1-[2-alkylthio-1-cyano-2-(phenacylthio)vinyl]-3,5-dimethylpyridinium bromides with a base and a dehydrogenating agent.

RESULTS AND DISCUSSION

When the corresponding pyridinium bromides (**3a**—**f**), which were prepared by the *S*-alkylation of 3,5-dimethylpyridinium 1-cyano-2-methylthio- (**1a**) and 1-cyano-2-ethylthio-2-thioxoethylide (**1**a) with phenacyl bromide (**2a**), *p*-chlorophenacyl bromide (**2b**), and *p*-bromophenacyl bromide (**2c**) at room temperature for 2h (Method A), were treated with 1,8-diazabicyclo[5.4.0]undec-1-ene (DBU) and then chloranil in chloroform at 0 ^{o}C for 4h, two types of products **5a**—**f** and **6a**—**f** were obtained in 53—67% and 2—9% yields, respectively. Similar treatment of pyridinium salts **3a**—**f** prepared from **1a,b** and **2a**—**c** in chloroform under the refluxing temperature for 1d (Method B) afforded the significant increased yields (10—22%) of the latter compounds **6a**—**f** with a reduction of the former ones **5a**—**f**. These results are shown in Scheme 1. As described above, we initially thought that major products **5a**—**f** must be 1-arylcarbonyl-6,8-dimethyl-2-(methylthio)indolizine-3-carbonitriles (**4**) which are formed *via* the ring contraction-desulfurization route of the transient 1-(arylcarbonyl)-7,9-dimethylpyrido[2,1-*c*]-1,4-thiazine-4-carbonitrile intermediates. However, their spectral and elemental analyses clearly indicated that **5a**—**f** are instead the ring contraction-rearrangement products, 1-arylcarbonylthio-6,8-dimethyl-2-(methylthio)indolizine-3-carbonitriles, and the X-ray analysis for one compound **5a** distinctly supported this structure. The ORTEP drawing[5] of compound **5a** is shown in Figure 1. On the other hand, minor products **6a**—**f** were obtained as very strong fluorescent substances and had the same compositions as the major products **5a**—**f** as exhibited in elemental analyses. The ^{1}H-NMR spectra of **6a**—**f** showed the signal characteristics of the protons and the methyl protons on the pyridine ring of the indolizine skeleton at δ 7.09—7.14 and 8.23—8.41 and at δ 2.30—2.34 and 2.49—2.51 respectively together with the signals for an arylcarbonyl group and a methythio or ethylthio group, but IR spectra did not show any cyano absorption bands near 2200 cm^{-1}. In addition, a largely shifted absorption band for an arylcarbonyl



Salt	React.	Ar	R	Products (%) A	Products (%) B
3a	1a+2a	Ph	Me	5a (67)+6a (2)	5a (46)+6a (10)
3b	1a+2b	*p*-ClC_6H_4	Me	5b (59)+6b (3)	5b (38)+6b (17)
3c	1a+2c	*p*-BrC_6H_4	Me	5c (65)+6c (4)	5c (38)+6c (21)
3d	1b+2a	Ph	Et	5d (57)+6d (3)	5d (37)+6d (22)
3e	1b+2b	*p*-ClC_6H_4	Et	5e (56)+6e (6)	5e (24)+6e (18)
3f	1b+2c	*p*-BrC_6H_4	Et	5f (53)+6f (9)	5f (20)+6f (21)

Scheme 1

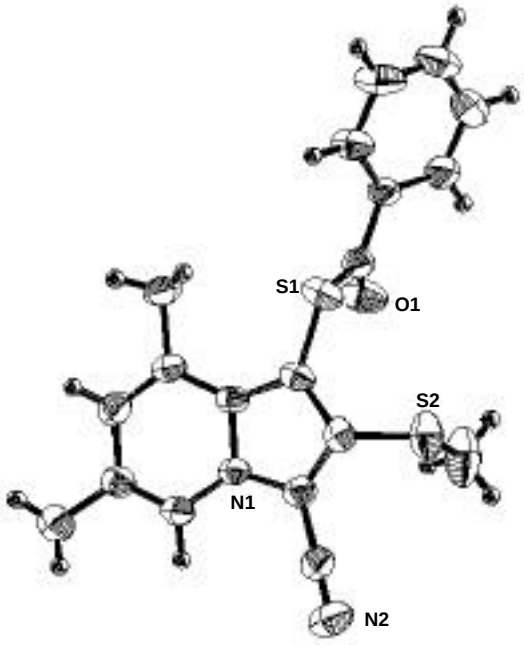
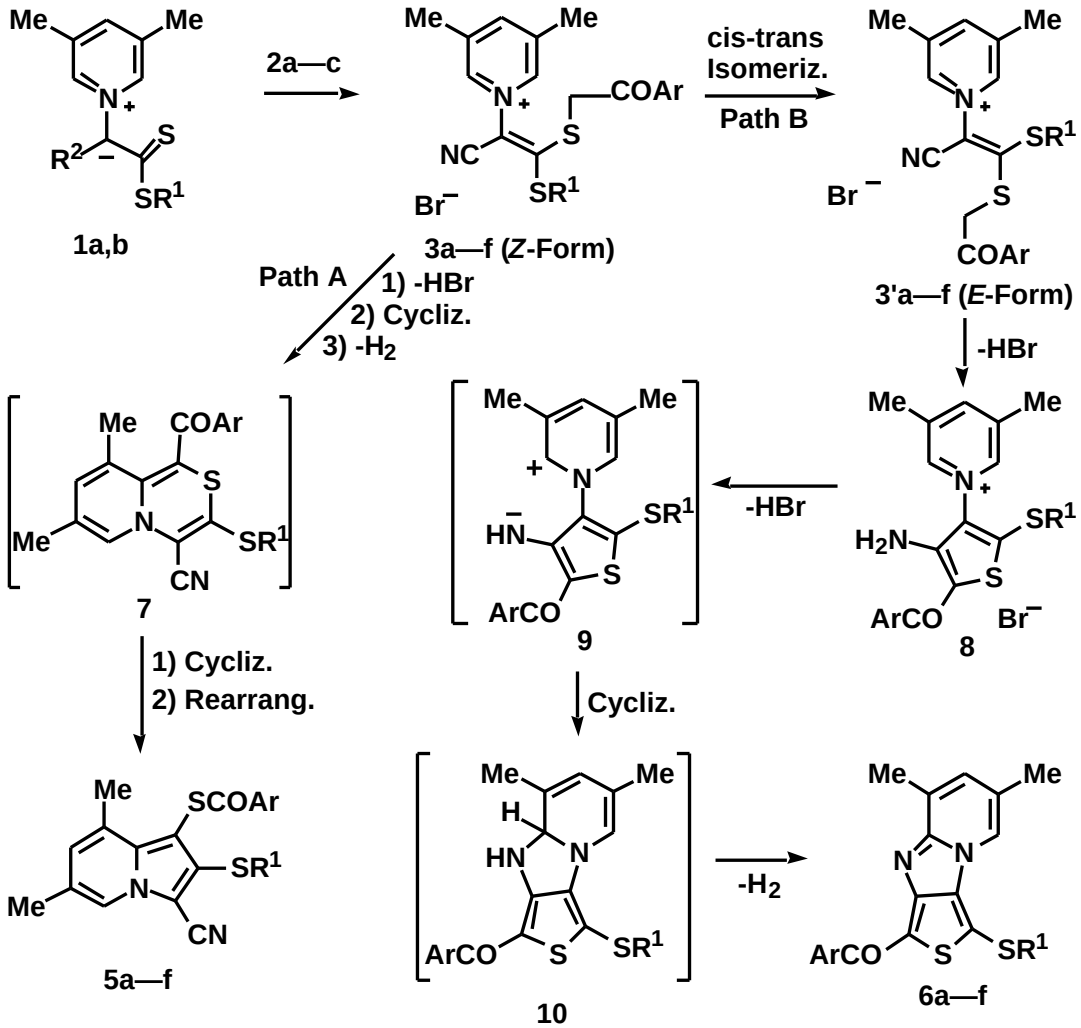


Figure 1. ORTEP drawing of 3a

group appeared at 1578—1607 cm^{-1}. Such largely lowered carbonyl absorption bands have been observed for the 2-arylcarbonyl groups on the five-membered heteroaromatics such as furans and thiophenes.[6,7] The structures for minor products **6a**—**f** were mainly determined from the mechanistic consideration which involves the disappearance of a cyano group and the possibility of the formation of a heteroaromatic thiophene ring from the corresponding pyridinium salts **3a**—**f** in these reactions. Possible reaction mechanisms for these reactions are indicated in Scheme 2. The *S*-alkylations of pyridinium ylides **1a**,**b** with phenacyl bromides **2a**—**c** afford the corresponding pyridinium salts **3a**—**f** with a *Z*-form in relation to the 1-vinyl group, from which 2-alkylthio-1-arylcarbonylthio-6,8-dimethylindolizine-3-carbonitriles (**5a**—**f**) were formed via the 1-arylcarbonyl-7,9-dimethylpyrido[2,1-*c*]-1,4-thizine-4-carbonitrile intermediate (**7**) (Path A). On the other hand, thermal *cis-trans* isomerization



Scheme 2

of **3a**—**f** to **3'a**—**f** having the *E*-form followed by the nucleophilic addition of the carbanion, generated under the reaction conditions employed here, on the intramolecular cyano group may lead to 1-[2-alkylthio-4-amino-5-(arylcarbonyl)thiophen-3-yl]-3,5-dimethylpyridinium bromides (**8**). Dehydrohalogenation of pyridinium salts **8** by a base, a 1,5-dipolar cyclization of the resulting pyridinium betaines **9**, and subsequent aromatization of the primary adducts **10** should give the title compounds **6a**—**f** (Path B). The increased formation of products **6a**—**f** under the heating conditions (Method B) supported also our proposed mechanism. To the best of my knowledge the formation of only one thieno[3',4':4,5]imidazo[1,2-*a*]pyridine derivative by the treatment of 1-[4-amino-5-cyano-2-(methylthio)thiophen-3-yl]pyridinium iodide with sodium hydride in refluxing tetrahydrofuran has been reported by Tominaga *et al.*[8] and this fact seems to be consistent with the formation mechanism for products **6a**—**f** proposed by us. The structures of **6a**—**f** were finally confirmed by the X-ray analysis of one compound **6a**. The ORTEP drawing[5] of **6a** is shown in Figure 2.

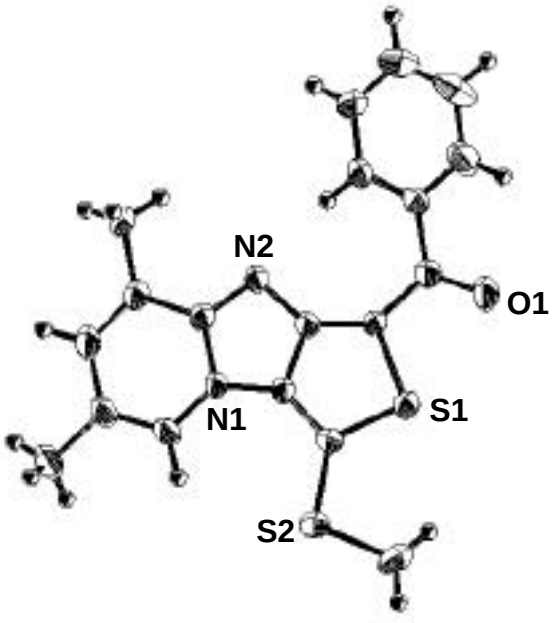


Figure 2. ORTEP drawing of compound 6a

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 JEOL JNM-LA400 (^{1}H: 400 MHz) spectrometer in deuteriochloroform with tetramethylsilane used as the internal standard; the chemical shifts are expressed in δ values. The IR spectra were taken with JASCO FT/IR-5300 IR spectrophotometers.

Reactions of pyridinium salts. General method. A mixture of 3,5-dimethylpyridinium 1-cyano-2-(*R*-thio)-2-thioxoethylide (**1**, 2 mmol) and phenacyl bromide (**2**, 2.1 mmol) was dissolved in chloroform (15 ml) and the resulting solution was kept at room temperature for 2h (Method A) or heated at the reflux temperature for 1d (Method B). The solution was then concentrated at reduced pressure and the residue was washed 3 times with ether to remove unaltered phenacyl bromide. Pyridinium salt was then dissolved in chloroform (30 ml) and allowed to react with DBU (0.302g, 2mmol) under stirring in an ice bath for 5 min. Chloranil (0.500g, 2 mmol) was then added to the resulting reaction mixture at that temperature and stirred for a further 4 h. The solution was concentrated at reduced pressure and the residual oil was separated by column chromatography on alumina using ether and then chloroform as an eluent. The collected ether fraction of 1-(benzoylthio)indolizine-3-carbonitrile (**5**) was concentrated at reduced pressure, and recrystallization from ethanol gave the pure product (**5**). The combined chloroform fraction with strong fluorescence was also concentrated at reduced pressure, and the crude theino[3',4':4,5]imidazo[1,2-*a*]pyridine (**6**) was purified by recrystallization from chloroform-ether. The respective yields in Methods A and B for these compounds (**5a**—**f** and **6a**—**f**) are shown in Scheme 1, and some other data are as follows:

1-Benzoylthio-6,8-dimethyl-2-(methylthio)indolizine-3-carbonitrile (**5a**): from **1a** and **2a**, colorless needles, mp 174—176 °C. IR (KBr): ν 1674, 2206 cm^{-1}. ^{1}H-NMR δ: 2.29 (s, 3H), 2.56 (s, 3H), 2.57 (s, 3H), 6.75 (br s, 1H), 7.50 (br t, *J*=7.6 Hz, 2H), 7.63 (br t, *J*=7,6 Hz, 1H), 7.98 (br s, 1H), 8.07 (br d, *J*=8.0 Hz, 2H). *Anal.* Calcd for $C_{19}H_{16}N_2OS_2$: C, 64.74; H, 4.58; N, 7.95. Found: C, 64.60; H, 4.53; N, 8.14.

1-(*p*-Chlorobenzoylthio)-6,8-dimethyl-2-(methylthio)indolizine-3-carbonitrile (**5b**): from **1a** and **2b**, colorless needles, mp 188—189 °C. IR (KBr): ν 1674, 2208 cm^{-1}. ^{1}H-NMR δ: 2.30 (3H, s, 6-Me), 2.56 (6H, s, SMe and 8-Me), 6.77 (1H, br s, 7-H), 7.48 (2H, br d, *J*=8.4 Hz, Ph-H), 8.00 (1H, br s, 5-H),

8.01 (2H, br d, *J*=8.4 Hz, Ph-H). *Anal.* Calcd for $C_{19}H_{15}ClN_2OS_2$: C, 58.98; H, 3.91; N, 7.24. Found: C, 59.18; H, 3.85; N, 6.97.

1-(*p*-Bromobenzoylthio)-6,8-dimethyl-2-(methylthio)indolizine-3-carbonitrile (**5c**): from **1a** and **2c**, colorless needles, mp 183—184 °C. IR (KBr): ν 1672, 2204 cm^{-1}. ^{1}H-NMR δ: 2.30 (3H, s, 6-Me), 2.56 (6H, s, SMe and 8-Me), 6.76 (1H, br s, 7-H), 7.65 (2H, br d, *J*=8.4 Hz, Ph-H), 7.94 (2H, br d, *J*=8.4 Hz, Ph-H), 7.99 (1H, br s, 5-H). *Anal.* Calcd for $C_{19}H_{15}BrN_2OS_2$: C, 52.90; H, 3.51; N, 6.49. Found: C, 53.03; H, 3.59; N, 6.29.

1-Benzoylthio-2-ethylthio-6,8-dimethylindolizine-3-carbonitrile (**5d**): from **1b** and **2a**, colorless needles, mp 133—135 °C. IR (KBr): ν 1674, 2202 cm^{-1}. ^{1}H-NMR δ: 1.26 (3H, t, *J*=7.2 Hz, $SCH_2\mathit{CH_3}$), 2.31 (3H, s, 6-Me), 2.59 (3H, s, 8-Me), 3.02 (2H, q, J=7.2 Hz, $S\mathit{CH_2}CH_3$), 6.75 (1H, br s, 7-H), 7.50 (2H, br t, *J*=7.6 Hz, Ph-H), 7.63 (1H, br t, *J*=7,6 Hz, Ph-H), 8.00 (1H, br s, 5-H), 8.07 (2H, br d, *J*=8.0 Hz, Ph-H). *Anal.* Calcd for $C_{20}H_{18}N_2OS_2$: C, 65.54; H, 4.95; N, 7.64. Found: C, 65.44; H, 4.87; N, 7.42.

1-(*p*-Chlorobenzoylthio)-2-ethylthio-6,8-dimethylindolizine-3-carbonitrile (**5e**): from **1b** and **2b**, colorless needles, mp 119—121 °C. IR (KBr) cm^{-1}: 1672, 2204. ^{1}H-NMR δ: 1.25 (3H, t, *J*=7.2 Hz, $SCH_2\mathit{CH_3}$), 2.30 (3H, s, 6-Me), 2.56 (3H, s, 8-Me), 2.98 (2H, q, J=7.2 Hz, $S\mathit{CH_2}CH_3$), 6.76 (1H, br s, 7-H), 7.48 (2H, br d, *J*=7.6 Hz, Ph-H), 8.00 (1H, br s, 5-H), 8.02 (2H, br d, *J*=8.0 Hz, Ph-H). *Anal.* Calcd for $C_{20}H_{17}ClN_2OS_2$: C, 59.91; H, 4.27; N, 6.99. Found: C, 60.19; H, 3.96; N, 6.71.

1-(*p*-Bromobenzoylthio)-2-ethylthio-6,8-dimethylindolizine-3-carbonitrile (**5f**): from **1b** and **2c**, colorless needles, mp 170—173 °C. IR (KBr) cm^{-1}: 1672, 2205. ^{1}H-NMR δ: 1.25 (3H, t, *J*=7.2 Hz, $SCH_2\mathit{CH_3}$), 2.31 (3H, s, 6-Me), 2.56 (3H, s, 8-Me), 2.98 (2H, q, J=7.2 Hz, $S\mathit{CH_2}CH_3$), 6.77 (1H, br s, 7-H), 7.65 (2H, br t, *J*=7.6 Hz, Ph-H), 7.94 (2H, br d, *J*=8.0 Hz, Ph-H), 8.01 (1H, br s, 5-H). *Anal.* Calcd for $C_{20}H_{17}BrN_2OS_2$: C, 53.93; H, 3.85; N, 6.29. Found: C, 53.84; H, 3.94; N, 6.29.

1-Benzoyl-6,8-dimethyl-3-(methylthio)thieno[3',4':4,5]imidazo[1,2-*a*]pyridine (**6a**): From **1a** and **2a**, orange prisms, mp 221—223 °C. IR (KBr) cm^{-1}: 1464, 1555, 1589. ^{1}H-NMR δ: 2.30 (3H, s, 6-Me), 2.49 (3H, s, 8-Me), 2.73 (3H, s, 3-SMe), 7.09 (1H, br s, 7-H), 7.49 (2H, br t, *J*=7.6 Hz, Ph-H), 7.56 (1H, br t, *J*=7,6 Hz, Ph-H), 8.23 (1H, br s, 5-H), 8.35 (2H, br d, *J*=7.2 Hz, Ph-H). *Anal.* Calcd for $C_{19}H_{16}N_2OS_2$: C, 64.74; H, 4.58; N, 7.95. Found: C, 64.90; H, 4.67; N, 7.71.

1-(*p*-Chlorobenzoyl)-6,8-dimethyl-3-(methylthio)thieno[3',4':4,5]imidazo[1,2-*a*]pyridine (**6b**): From **1a** and **2b**, yellow needles, mp 219—220 °C. IR (KBr) cm^{-1}: 1474, 1561, 1607. ^{1}H-NMR δ: 2.33 (3H, s, 6-Me), 2.51 (3H, s, 8-Me), 2.76 (3H, s, 3-SMe), 7.14 (1H, br s, 7-H), 7.47 (2H, br d, *J*=7.6 Hz, Ph-H), 8.26 (1H, br s, 5-H), 8.39 (2H, br d, *J*=7.2 Hz, Ph-H). *Anal.* Calcd for $C_{19}H_{15}ClN_2OS_2$+H_2O: C, 56.36; H, 4.23; N, 6.92. Found: C, 56.55; H, 4.37; N, 6.69.

1-(*p*-Bromobenzoyl)-6,8-dimethyl-3-(methylthio)thieno[3',4':4,5]imidazo[1,2-*a*]pyridine (**6c**): From **1a** and **2c**, yellow needles, mp 225—228 °C. IR (KBr) cm^{-1}: 1472, 1561, 1586. ^{1}H-NMR δ: 2.34 (3H, s, 6-Me), 2.52 (3H, s, 8-Me), 2.77 (3H, s, 3-SMe), 7.14 (1H, br s, 7-H), 7.63 (2H, br d, *J*=7.6 Hz, Ph-H), 8.26 (1H, br s, 5-H), 8.30 (2H, br d, *J*=7.2 Hz, Ph-H). *Anal.* Calcd for $C_{19}H_{15}BrN_2OS_2$: C, 52.90; H, 3.51; N, 6.49. Found: C, 52.82; H, 3.76; N, 6.32.

1-Benzoyl-3-ethylthio-6,8-dimethylthieno[3',4':4,5]imidazo[1,2-*a*]pyridine (**6d**): From **1b** and **2a**, yellow needles, mp 199—201 °C. IR (KBr) cm^{-1}: 1464, 1554, 1589. ^{1}H-NMR δ: 1.43 (3H, t, *J*=7.2 Hz, $SCH_2\mathit{CH_3}$), 2.33 (3H, s, 6-Me), 2.52 (3H, s, 8-Me), 3.13 (2H, q, *J*=7.2 Hz, $S\mathit{CH_2}CH_3$), 7.13 (1H, br s, 7-H), 7.50 (2H, br t, *J*=7.6 Hz, Ph-H), 7.57 (1H, br t, *J*=7,6 Hz, Ph-H), 8.33 (2H, br d, *J*=7.2 Hz, Ph-H), 8.41 (1H, br s, 5-H). *Anal.* Calcd for $C_{20}H_{18}N_2OS_2$: C, 65.54; H, 4.95; N, 7.64. Found: C, 65.57; H, 4.86; N, 7.71.

1-(*p*-Chlorobenzoyl)-3-ethylthio-6,8-dimethylthieno[3',4':4,5]imidazo[1,2-*a*]pyridine (**6e**): From **1b** and **2b**, orange needles, mp 209—211 °C. IR (KBr) cm^{-1}: 1464, 1560, 1580. ^{1}H-NMR δ: 1.45 (3H, t, *J*=7.2 Hz, $SCH_2\mathit{CH_3}$), 2.33 (3H, s, 6-Me), 2.51 (3H, s, 8-Me), 3.15 (2H, q, *J*=7.2 Hz, $S\mathit{CH_2}CH_3$), 7.13 (1H, br s, 7-H), 7.47 (2H, br d, *J*=7.6 Hz, Ph-H), 8.37 (2H, br d, *J*=7.2 Hz, Ph-H), 8.38 (1H, br s, 5-H). *Anal.* Calcd for $C_{20}H_{17}ClN_2OS_2$: C, 59.91; H, 4.27; N, 6.99. Found: C, 60.16; H, 4.14; N, 6.88.

1-(*p*-Bromobenzoyl)-3-ethylthio-6,8-dimethylthieno[3',4':4,5]imidazo[1,2-*a*]pyridine (**6f**): From **1b** and **2c**, orange prisms, mp 230—232 °C. IR (KBr) cm^{-1}: 1464, 1537, 1578. ^{1}H-NMR δ: 1.45 (3H, t, *J*=7.2 Hz, $SCH_2\mathit{CH_3}$), 2.34 (3H, s, 6-Me), 2.52 (3H, s, 8-Me), 3.15 (2H, q, *J*=7.2 Hz, $S\mathit{CH_2}CH_3$), 7.14 (1H, br s, 7-H), 7.63 (2H, br t, *J*=7.6 Hz, Ph-H), 8.30 (2H, br d, *J*=7.2 Hz, Ph-H), 8.38 (1H, br s, 5-H). *Anal.* Calcd for $C_{20}H_{17}BrN_2OS_2$: C, 53.93; H, 3.85; N, 6.29. Found: C, 54.07; H, 3.96; N, 6.04.

Crystallography of 1-benzoylthio-6,8-dimethyl-2-(methylthio)indolizine-3-carbonitrile (5a) A brown prismatic single crystal (0.46x0.46x0.38mm) grown from chloroform-ether was used for the unit-cell determinations and data collection by a Rigaku AFC5S four-circle diffractometer with graphite-monochromated MoK_α radiation (λ=0.71069 Å). The crystal data of this compound are as follows: **5a**: $C_{19}H_{16}N_2OS_2$; *M*=352.47; triclinic, space group $P\bar{1}$(#2), *Z*=2 with *a*=10.526 (8) Å, *b*=10.929 (13) Å, *c*=8.313 (79) Å, α=100.79 (9)°, β=110.56 (5)°; γ=78.95 (9)°,*V*=871.3 (14) Å^3 and $D_{calc.}$=1.343 g/cm^3. All calculations were performed using CrystalStructure.[9] The structure was solved by a direct method (SIR).[10] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were attached at the idealized position and not refined. The final *R*- and R_w-factors after full-matrix least-squares refinements were 0.054 and 0.045 respectively for 3143 (I>2.00σ(I)) observed reflections.

Crystallography of 1-benzoyl-6,8-dimethyl-3-(methylthio)thieno[3',4':4,5]imidazo[1,2-*a*]indolizine (6a) An orange prismatic single crystal (0.88x0.82x0.16mm) grown from chloroform-ether was used for the unit-cell determinations and data collection by a Rigaku AFC5S four-circle diffractometer with graphite-monochromated MoK_α radiation (λ=0.71069 Å). The crystal data of this compound are as follows: **6a**: $C_{19}H_{16}N_2OS_2$; *M*=352.47; triclinic, space group $P\bar{1}$(#2), *Z*=2 with *a*=9.953 (14) Å, *b*=10.86 (2) Å, *c*=9.458 (9) Å, α=109.49 (12)°, β=94.79 (10)°; γ=116.05 (14)°,*V*=833.6 (22) Å^3 and $D_{calc.}$=1.404 g/cm^3. All calculations were performed using CrystalStructure.[9] The structure was solved by a direct method (SIR).[10] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were attached at the idealized position and not refined. The final *R*- and R_w-factors after full-matrix least-squares refinements were 0.092 and 0.082 respectively for 2900 (I>2.00σ(I)) observed reflections.

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