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Reactions of 2-Dialkylamino-5-phenyl-1,3-oxathiolium Cation with Nucleophiles Containing an Amino Group[1]

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Reactions of 2-dialkylamino-1,3-oxathiolium (I) with amino-nucleophiles provide simple access to a variety of heterocyclic compounds. Thiadiazines and thiazoles were readily obtained from the reaction with hydrazines and ammonia, respectively. The intermediates, which were easily converted into thiazoles, were also isolated. Study of the reaction of I with aromatic amines revealed the formation of ring-opened ketones and 2-arylimino-1,3-oxathioles depending upon the reaction conditions. Reactions of I with aromatic and aliphatic amines in boiling glacial acetic acid resulted in the formation of 2-iminothiazoline derivatives.

Keywords——heterocyclic synthesis; thiazole; thiazoline; thiadiazine; 6π conjugated system with three hetero atoms

1,3-Oxathiolium cation is a member of a 6π conjugated system with a positive charge on the five-membered ring. A C-2 carbon is bonded with three hetero atoms leading to a stable cation in which the resonance contribution of the tertiary iminium structure (I) is predominant.[3] We have shown that the reaction of I with active methylene compounds in the presence of base gives the ring-opened addition products,[4] 1,3-oxathiol-2-ylidenes,[4] or thiophenes[5] depending on the nature of the reagents and reaction conditions.

We now report a convenient method for synthesizing a variety of heterocyclic compounds from I and nucleophiles containing an amino group.

When 5-phenyl-2-piperidino-1,3-oxathiolium hydrogen sulfate (Ia)[3] was allowed to react with an excess of hydrazine hydrate in aqueous solution at room temperature, yellow prisms of mp 92—93° were obtained in an excellent yield (96%). The structure of this product was confirmed to be 5-phenyl-2-piperidino-6H-1,3,4-thiadiazine (IIa) by spectral data and an unequivocal synthesis from phenacyl bromide and piperidinothiosemicarbazide.[6] 6H-1,3,4-Thiadiazine (II) is useful for the synthesis of pyrazole derivatives by desulfurization.[7]

When 2-dimethylamino-5-phenyl-1,3-oxathiolium hydrogen sulfate[3,8] was allowed to react with hydrazine hydrate as described above, 2-dimethylamino-6H-1,3,4-thiadiazine (IIc)[9] was obtained.

A similar reaction occurred with an excess of phenylhydrazine in methylene chloride solution, from which 4,5-diphenyl-2-piperidino-1,3-thiadiazine (IIIa), mp 128—131°, was obtained in 61% yield.

1) This paper forms Part XII of a series of "Studies on Heterocyclic Cation Systems." Part XI: K. Hirai, H. Sugimoto, and T. Ishiba, *Chem. Pharm. Bull.* (Tokyo), **25**, 2292 (1977). A part of this paper was reported in a preliminary form: K. Hirai and T. Ishiba, *Chem. Commun.*, **1971**, 1318.
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When 28% aqueous ammonia was added to an aqueous solution of Ia under ice-cooling, crystals were obtained in 85% yield. Although analysis indicated that these contained one H_2O more than 5-phenyl-2-piperidinothiazole (Va), on attempted recrystallization from ethyl acetate the substance was readily converted into Va, colorless prisms of mp 74—75°. The unstable intermediate obtained would be in a ring-chain tantomeric equilibrium (IV and IV'),[10] but the posibility of its taking the structure of IV'' or IV''' can not be ruled out. Treatment of this unstable intermediate with ethanolic hydrogen chloride immediately gave thiazole hydrochloride.

Similarly, 2-morpholino-5-phenylthiazole (Vb) and 2-dimethylamino-5-phenylthiazole (Vc) were obtained in good yield from cations Ib and Ic, respectively. The intermediates (IVb, c and/or IV'bc) were also isolated by careful treatment and converted readily into thiazoles (Vb, c). These thiazoles have been synthesized by other methods.[11] Recently, Hartmann also reported a similar reaction of 2-aryl-1,3-oxathiolium salts with nucleophiles leading to thiazole and thiophene derivatives.[12]

When Ia was allowed to react with arylamine in aqueous solution, 2-arylimino-1,3-oxathiole (VII) and the ring-opened addition product (VI) were obtained (Table I).

Table I. Reactions of Ia and Arylamines (1 : 3 Molar Ratio)

Ar	Solvent	VI (%)	mp (°C)	VII (%)	mp (°C)
Ph	CH_2Cl_2	99.5	Oil	—	—
Ph	H_2O	32	—	27	131—133[a]
C_6H_4-CH_3-*p*	CH_2Cl_2	96	43—44	—	—
C_6H_4-CH_3-*p*	H_2O	56.5		29.6	129—131
C_6H_4-Cl-*p*	CH_2Cl_2	88	81—83		

a) Ref. 13, mp 137—138°.

In methylene chloride solution, however, the reaction of Ia afforded VI exclusively. These reactions proceed smoothly and are general in scope for heterocyclic synthesis. Initial reaction takes place between the nitrogen of the nucleophiles and the C-2 position in the 1,3-oxathiole ring to give an adduct. Loss of a proton results in C–O bond cleavage to give the imino-ketone derivative, which is immediately trapped by intramolecular addition of the amino group to the carbonyl. The compound then undergoes dehydration to afford the 1,3,4-thiadiazine or the thiazole. In the case of the weak basic arylamine, however, proton transfer to the piperidino nitrogen followed by extrusion of the piperidine molecules gave the 2-arylimino-1,3-oxathiole.

Trisubstituted pyrylium salts can readily be converted into N-arylated pyridinium salts.[14] Reaction of 1,3,4-oxadiazolium salt with primary amines in glacial acetic acid gave 1,3,4-triazolium salt.[15] These results prompted us to investigate the reaction of I with aromatic and aliphatic amines in glacial acetic acid.

When the solution of 5-phenyl-2-piperidino-1,3-oxathiolium (Ia) perchlorate and two equivalents of aniline in glacial acetic acid was heated under reflux, 3,4-diphenyl-2-phenyl-

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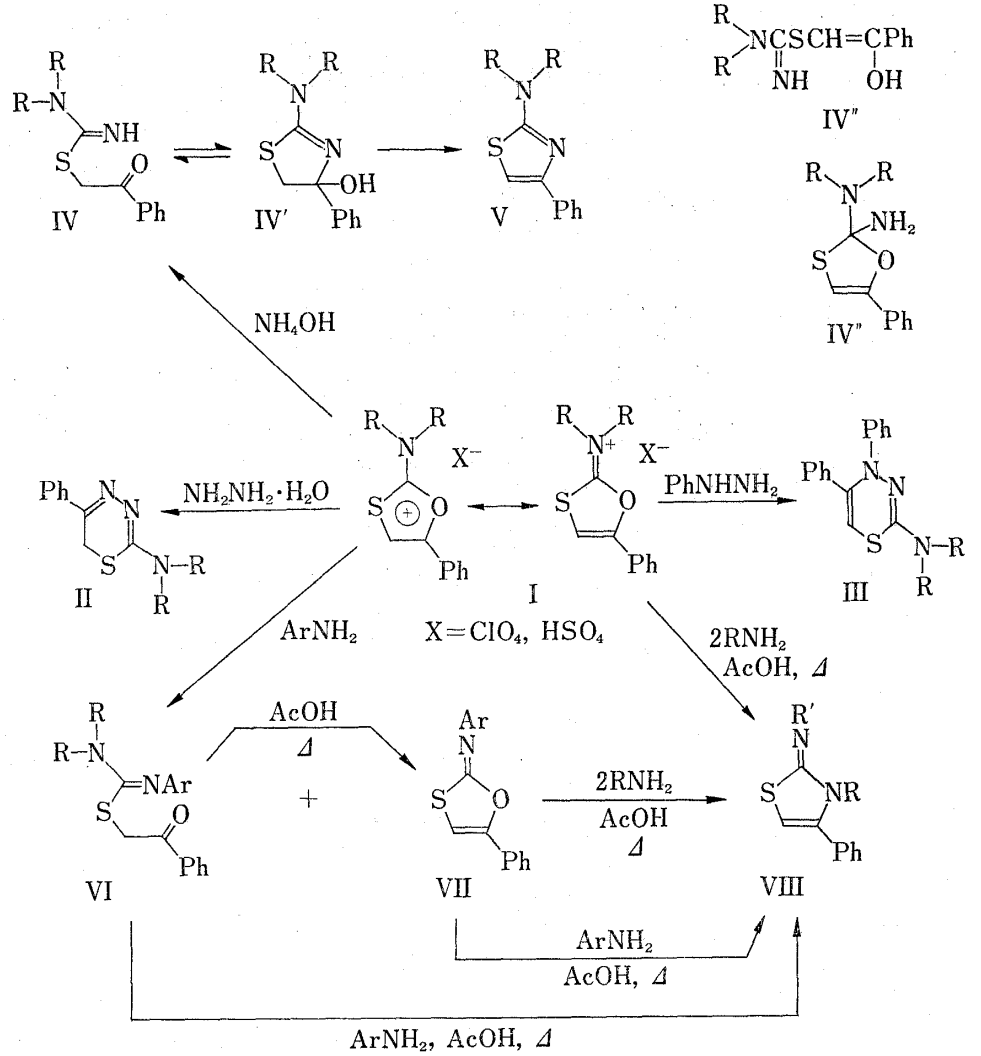
iminothiazoline (VIIIa) was obtained as a mixture of free base and its perchlorate in excellent yield. Similarly, heating with two equivalents of *n*-propylamine in glacial acetic acid gave 4-phenyl-3-*n*-propyl-2-*n*-propyliminothiazoline (VIIIb) in 85% yield.

Conversion of 1,3-oxathiole into thiazoline was also achieved by heating 5-phenyl-2-phenylimino-1,3-oxathiole (VIIa) hydrochloride with two equivalents of *n*-propylamine in glacial acetic acid under reflux, and 4-phenyl-2-phenylimino-3-*n*-propyl-thiazoline (VIIIc) hydrochloride, mp 211—213°, was obtained in 76% yield.

In order to study the pathway of this reaction, ring-opened addition product VI was also heated with *p*-toluidine in glacial acetic acid under reflux, 2-*p*-toluiminothiazoline VIIId was readily obtained. On the other hand, heating VI in glacial acid under reflux gave 2-arylimino-5-phenyl-1,3-oxathiole (VII), which was further converted into 3-aryl-2-arylimino-4-phenyl-thiazoline (VIII) by heating with arylamine in glacial acetic acid. Therefore, conversion of VI into thiazoline (VIII) could be expected to proceed *via* 1,3-oxathiole (VII).



I—VIa: $\begin{matrix}R\\R\end{matrix}\!>\!N\!-\!=\!\langle\,\rangle\!-N-$

I—VIb: $\begin{matrix}R\\R\end{matrix}\!>\!N\!-\!=\!O\!\langle\,\rangle\!-N-$

I—VIc: $\begin{matrix}R\\R\end{matrix}\!>\!N\!-\!=\!(CH_3)_2N-$

VIIa: Ar=Ph
VIIb: Ar=C_6H_4-CH_3-*p*

VIIIa: R=R'=Ph
VIIIb: R=R'=*n*-Pr
VIIIc: R=*n*-Pr,R'=Ph
VIIId: R=R'=C_6H_4-CH_3-*p*

Chart 1

Some 2-aryliminothiazolines have been reported to show antibacterial activity, and have been synthesized by several methods from thiourea derivatives.[16–19] Our method of obtaining 2-aryliminothiazoline might be interesting as an alternative which does not require the use of thiourea derivatives.

In summary, a variety of heterocyclic compounds were readily obtained from the reaction of 2-dialkylamino-1,3-oxathiolium salts (I) with various nucleophiles. Therefore, I is a new synthone of versatile utility.

Experimental

Melting points are uncorrected. Ultraviolet (UV) spectra were measured with a Hitachi EPS-2 spectrometer, infrared (IR) spectra in KBr with a JASCO DS-403G spectrometer, nuclear magnetic resonance (NMR) spectra on a Varian A-60 instrument with TMS as an internal standard, and mass spectra with RMU-6E mass spectrometer.

5-Phenyl-2-piperidino-6H-1,3,4-thiadiazine (IIa)——To a solution of 0.63 g of 80% $NH_2NH_2 \cdot H_2O$ in 5 ml of H_2O, 0.85 g of 5-phenyl-2-piperidino-1,3-oxathiolium hydrogen sulfate (Ia)[3] was added and stirred for 1 hr at room temperature. The resulting yellow crystals were collected by filtration to give 0.62 g (95.5%) of IIa. Recrystallization from ether gave yellow plates of mp 92—93°. *Anal.* Calcd. for $C_{14}H_{17}N_3S$: C, 64.83; H, 6.61; N, 16.20; S, 12.36. Found: C, 64.74; H, 6.68; N, 16.16; S, 12.63. UV λ_{max}^{EtOH} 226, 260, 286, 347 nm (log ε 4.08, 3.99, 3.90, 3.96). NMR ($CDCl_3$) δ: 1.65 (6H, broad, s, piperidino), 3.53 (2H, s, CH_2), 3.73 (4H, broad, m, piperidino), 7.30—7.55, 7.68—8.03 (5H, m, Ph). IR ν_{max}^{KBr} cm^{-1}: 1500. MS *m/e*: 128 (base ion peak).

2-Dimethylamino-5-phenyl-6H-1,3,4-thiadiazine (IIc)——To a solution of 0.42 ml of 80% $NH_2NH_2 \cdot H_2O$ in 5 ml of H_2O, 1.01 g of 2-dimethylamino-5-phenyl-1,3-oxathiolium hydrogen sulfate (Ic)[3] was added under ice-cooling and stirred for 1 hr. Resulting crystals were collected to give 0.35 g (41%) of IIc, which was identical with the sample prepared as described in ref. 9.

4,5-Diphenyl-2-piperidino-1,3,4-thiadiazine (IIIa)——A solution of 0.85 g of Ia (hydrogen sulfate) and 0.81 g of phenylhydrazine in 35 ml of CH_2Cl_2 was stirred for 1 hr at room temperature. To the reaction mixture, H_2O was added and the CH_2Cl_2 layer was separated. The CH_2Cl_2 layer was dried over $MgSO_4$ and evaporated the solvent. The residue was purified by silica gel column chromatography eluted with $CHCl_3$. Recrystallization of the isolated crystals from *n*-hexane gave 0.51 g (61%) of IIIc as yellow pillars of mp 120—123°. *Anal.* Calcd. for $C_{20}H_{21}N_3S$: C, 71.60; H, 6.31; N, 12.53; S, 9.56. Found: C, 71.87; H, 6.62; N, 12.46; S, 9.84. UV λ_{max}^{EtOH} 210 (sh), 241, 267, 295 (sh), 320 (sh), 352 (sh) nm (log ε 4.32, 4.13, 4.30, 3.98, 3.80, 3.49). NMR ($CDCl_3$)δ: 1.63 (6H, broad, s, piperidino), 3.55 (4H, broad, m, piperidino), 5.60 (1H, s, CH=), 6.98 (5H, s, Ph), 7.18 (5H, s, Ph). MS *m/e*: 335 (M^+).

4-Phenyl-2-piperidinothiazole (Va)——To a solution of 2.25 g of Ia (hydrogen sulfate) in 5 ml of H_2O, 3.3 g of 28% NH_4OH was added dropwise under ice-cooling. The separated oil was extracted with $CHCl_3$, and the $CHCl_3$ extract was dried over $MgSO_4$ and concentrated *in vacuo* to give 1.48 g (85%) of IVa and/or IVa′. Recrystallization from AcOEt gave colorless plates of mp 90—106°. *Anal.* Calcd. for $C_{14}H_{18}N_2OS$: C, 64.09; H, 6.91; N, 10.68; S, 12.23. Found: C, 64.00; H, 6.91; N, 10.73; S, 12.40.

After refluxing the solution of above crystals in AcOEt for 30 min, AcOEt was removed and the residue was recrystallized from petroleum benzine to give Va as colorless prisms of mp 74—75°. *Anal.* Calcd. for $C_{14}H_{16}N_2S$: C, 68.81; H, 6.60; N, 11.47; S, 13.12. Found: C, 69.08; H, 6.42; N, 11.45; S, 13.26. UV λ_{max}^{EtOH} 239, 265 (sh), 287 nm (log ε 4.41, 4.06, 3.87). NMR ($CDCl_3$) δ: 1.67 (6H, broad, s, piperidino), 3.50 (4H, broad, m, piperidino), 6.70 (1H, s, CH=).

Suspension of IVa and/or IVa′ in EtOH, conc. HCl was added. Addition of AcOEt to the resulting clear solution gave colorless needles of V–HCl, mp 190—193°. *Anal.* Calcd. for $C_{14}H_{17}N_2SCl$: C, 59.88; H, 6.16; N, 9.98; S, 11.41; Cl, 12.01. Found: C, 59.75; H, 6.05; N, 9.88; Cl, 12.14.

4-Phenyl-2-morpholinothiazole (Vb)——To a solution of 0.69 g of Ib (hydrogen sulfate) in 5 ml of H_2O, 1 g of 28% NH_4OH was added and stirred for 30 min at room temperature. Separated solid was extracted with $CHCl_3$, and the $CHCl_3$ extract was dried over $MgSO_4$ and concentrated *in vacuo* to give 0.48 g (90.6%) of IV and/or IV′. Recrystallization from ether gave colorless pillars of mp 90—112°. *Anal.* Calcd. for $C_{13}H_{16}N_2O_2S$: C, 59.07; H, 6.10; N, 10.60; S, 12.13. Found: C, 59.47; H, 6.12; N, 10.62; S, 12.23.

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The solution of these crystals in AcOEt was refluxed for 30 min and AcOEt was removed. Recrystallization of the residue from *n*-hexane gave Vb as colorless prisms of mp 79—80°. *Anal.* Calcd. for $C_{13}H_{14}N_2OS$: C, 63.39; H, 5.73; N, 11.37; S, 13.01. Found: C, 63.23; H, 5.70; N, 11.37; S, 13.02. UV λ_{max}^{EtOH} 242.5, 266 (sh), 283 nm (log ε 4.41, 4.03, 3.84).

2-Dimethylamino-4-phenylthiazole (Vc)——To a solution of 0.76 g Ic (hydrogen sulfate) in 5 ml of H_2O, 1.24 g of 28% NH_4OH was added and stirred for 30 min at room temperature. Separated oil was solidified and collected by filtration to give 0.5 g (89%) of IVc and/or IVc'.

Attempted recrystallization from EtOH gave Vc as pale yellow oil. *Anal.* Calcd. for $C_{11}H_{12}N_2S$: C, 64.67; H, 5.92; N, 13.71; S, 15.70. Found: C, 64.78; H, 5.54; N, 13.77; S, 15.92. UV λ_{max}^{EtOH} 237, 265 (sh), 289 nm (log ε 4.42, 3.98, 3.82).

N-(4-Phenyl-1,3-oxathiol-2-yliden)phenylamine (VIIa) and N-[Phenylketomethylthio(piperidino)methylidene]phenylamine (VIa: Ar=Ph)——a) To a solution of 0.7 g of aniline in 10 ml of H_2O, 0.85 g of Ia (hydrogen sulfate) was added. Separated crystals were extracted with $CHCl_3$. The $CHCl_3$ extract was washed with H_2O, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was treated with *n*-hexane to give 0.17 g (27%) of VIIa, which was recrystallized from ether to give colorless prisms up mp 131—133°. *Anal.* Calcd. for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.53; S, 12.65. Found: C, 71.43; H, 4.11; N, 5.68; S, 12.74. UV λ_{max}^{EtOH} 212.2, 283 (sh), 297 (sh) nm (log ε 4.33, 4.31, 4.36). NMR ($CDCl_3$) δ: 6.35 (CH=). *n*-Hexane filtrate was concentrated *in vacuo* and the residue was purified by silica gel column chromatography with ether. VIa was obtained as colorless oil (0.27 g, 32%). *Anal.* Calcd. for $C_{20}H_{22}N_2OS$: C, 70.97; H, 6.55; N, 8.28; S, 9.48. Found: C, 71.04; H, 6.33; N, 7.95; S, 9.74. UV λ_{max}^{EtOH} 235.5, 248, 348 nm (log ε 4.37, 4.34, 3.72).

b) To a solution of 0.7 g of aniline in 20 ml of CH_2Cl_2, 0.85 g of Ia hydrogen sulfate was added. After stirring for 1.5 hr at room temperature, H_2O was added and extracted with $CHCl_3$. The $CHCl_3$ extract was dried over $MgSO_4$ and concentrated *in vacuo* to give 0.8 g (99.5%) of VIa as colorless oil.

N-(4-Phenyl-1,3-oxathiol-2-yliden)-4-methylphenylamine (VIIb) and N-[Phenylketomethylthio(piperidino)-methylidene]-4-methylphenylamine (VIa: Ar=C_6H_4-CH_3-*p*)——a) To a solution of 0.8 g of *p*-toluidine in 10 ml of H_2O, 0.85 g of Ia (hydrogen sulfate) was added. After stirring for 2 hr at room temperature, the reaction mixture was extracted with $CHCl_3$. The $CHCl_3$ extract was washed with H_2O, dried, and concentrated *in vacuo*. The residue was treated with *n*-hexane to give 0.20 g (30%) of VIIb, which was recrystallized from AcOEt to give colorless pillars of mp 129—131°. *Anal.* Calcd. for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.24; S, 11.99. Found: C, 71.65; H, 4.64; N, 5.09; S, 12.32. UV λ_{max}^{EtOH} 223, 295 nm (log ε 4.31, 4.29). NMR ($CDCl_3$) δ: 2.23 (3H, s, CH_3), 6.35 (1H, s, CH=).

n-Hexane filtrate was concentrated *in vacuo* and the residue was purified by silica gel column chromatography with ether–*n*-hexane (1: 1) to give 0.50 g (56.5%) of VIa (Ar=C_6H_4–CH_3-*p*) as colorless crystals of mp 43—44°. *Anal.* Calcd. for $C_{21}H_{24}N_2OS$: C, 71.53; H, 6.86; N, 7.95; S, 9.10. Found: C, 71.66; H, 6.79; N, 8.09; S, 9.52. UV λ_{max}^{EtOH} 245, 280 (sh), 344 nm (log ε 4.32, 2.94, 3.60). NMR ($CDCl_3$) δ: 2.25 (3H, s, CH_3), 3.90 (2H, s, CH_2).

b) To a solution of 0.8 g of *p*-toluidine in 20 ml of CH_2Cl_2, 0.85 g of Ia hydrogen sulfate was added. After stirring for 2 hr at room temperature, H_2O was added and extracted with $CHCl_3$. The $CHCl_3$ extract was dried over $MgSO_4$, evaporated, and the residue was purified by silica gel column chromatography to give 0.84 g (96%) of VIa (Ar=C_6H_4–CH_3-*p*).

N-[Phenylketomethylthio(piperidino)methylidene]-4-chlorophenylamine (VIa: R=C_6H_4-Cl-*p*)——To a solution of 0.96 g of *p*-chloroaniline in 20 ml of CH_2Cl_2, 0.85 g of Ia hydrogen sulfate was added. After stirring for 2 hr at room temperature, H_2O was added and extracted with CH_2Cl_2. The CH_2Cl_2 extract was dried over $MgSO_4$, concentrated *in vacuo*, and the residue was purified by silica gel column chromatography with ether–*n*-hexane (1: 1) to give 0.82 g (88%) of VIa (R=C_6H_4–Cl-*p*) as pale yellow crystals of mp 81—83°. *Anal.* Calcd. for $C_{20}H_{21}ClN_2OS$: C, 64.42; H, 5.68; N, 7.51; S, 8.60. Found: C, 64.32; H, 5.65; N, 7.39; S, 8.67. UV λ_{max}^{EtOH} 238, 245, 285 (sh) nm (log ε 4.42, 4.42, 4.10).

N-[3,4-Diphenylthiazolin-2-ylidene]phenylamine (VIIIa)——A mixture of Ia (perchlorate) and 0.56 g of aniline in 6 ml of glacial acetic acid was refluxed for 15 min. After cooling, ether was added to the reaction mixture and the resulting crystals of VIIIa hydrogen perchlorate (including free VIIIa) were collected (1.25 g). These crystals were suspended in 30 ml of EtOH and 2 g of Et_3N was added. After stirring for 8 hr, the resulting free VIIIa, mp 188—190°, were collected. Yield 0.89 g (90%). *Anal.* Calcd. for $C_{21}H_{16}N_2S$: C, 76.80; H, 4.91; N, 8.53; S, 9.77. Found: C, 76.58; H, 4.91; N, 9.01; S, 10.41. UV λ_{max}^{EtOH} 228 (sh), 272 (sh), 298 nm (log ε 4.35, 4.01, 4.08).

N-[4-Phenyl-3-*n*-propylthiazolin-2-ylidene]-*n*-propylamine (VIIIb)——To a solution of Ia (hydrogen sulfate) in 8 ml of glacial acetic acid, 0.89 g of *n*-propylamine was added and refluxed for 10 min. After concentration of the reaction mixture *in vacuo*, the residue was treated with ether and aq. $NaHCO_3$ solution. The ether layer was dried over $MgSO_4$ and concentrated *in vacuo* to give 1.1 g (85%) of VIIIb as colorless oil. The oil was treated with EtOH–HCl to give VIIIb–HCl. Recrystallization from acetone gave colorless crystals of mp 176—178°. *Anal.* Calcd. for $C_{15}H_{21}ClN_2S$: C, 60.69; H, 7.13; Cl, 11.95; N, 9.44; S, 10.81. Found: C, 60.92; H, 7.07;; Cl, 12.09 N, 9.55; S, 10.98.

N-[4-Phenyl-3-*n*-propylthiazolin-2-ylidene]phenylamine (VIIIc)——A mixture of 0.87 g of VIIa–HCl and 0.35 g of *n*-propylamine in 4 ml of glacial acetic acid was refluxed for 15 min. After cooling, ether was

added to the reaction mixture and the resulting n-$PrNH_2 \cdot HCl$ (0.22 g) was removed by filtration. The filtrate was concentrated *in vacuo* and the residual oil was purified by silica gel column chromatography with ether. Treatment of the separated oil with 3 ml of 10% EtOH–HCl gave 0.75 g (76%) of VIIIc–HCl as colorless crystals of mp 211—213°. *Anal.* Calcd. for $C_{18}H_{19}ClN_2S$: C, 65.34; H, 5.79; Cl, 10.71; N, 8.46; S, 9.69. Found: C, 65.80; H, 5.83; Cl, 10.85; N, 8.09; S, 9.72. UV λ_{max}^{EtOH} 230 (sh), 265, 290 nm (log ε 4.24, 4.01, 4.05).

N-[3-(4-Methylphenyl)-4-phenylthiazolin-2-ylidene]-4-methylphenylamine (VIIId)——a) A solution of 0.7 g of VIa (Ar=C_6H_4–CH_3-p) and 0.24 g of p-toluidine in 4 ml of glacial acetic acid was refluxed for 10 min. The reaction mixture was concentrated *in vacuo*, the residue was treated with aq. $NaHCO_3$ solution, and extracted with $CHCl_3$. The $CHCl_3$ extract was dried over $MgSO_4$, concentrated *in vacuo*, and the residue was treated with ether to give 0.57 g (78%) of VIIId. Recrystallization from AcOEt gave colorless crystals of mp 188—189°. *Anal.* Calcd. for $C_{23}H_{20}N_2S$: C, 77.49; H, 5.66; N, 7.86; S, 9.00. Found: C, 77.92; H, 5.70; N, 8.04; S, 9.16. UV λ_{max}^{EtOH} 230 (sh), 275 (sh), 298 nm (log ε 4.37, 4.06, 4.11).

b) A solution of VIa (Ar=C_6H_4–CH_3-p) in 4 ml of glacial acetic acid was refluxed for 10 min. The reaction mixture was concentrated *in vacuo*, and the residue was treated with ether and aq. $NaHCO_3$ solution. The ether layer was dried over $MgSO_4$, concentrated *in vacuo*, and the residue was treated with n-hexane to give 0.36 g (67.5%) of VIIb. To a solution of 0.4 g of VIIb in 3 ml of glacial acetic acid, 0.18 g of p-toluidine was added and refluxed for 10 min. The reaction mixture was concentrated *in vacuo* and the residue was treated with n-hexane to give 0.51 g (96%) of VIIId.