[Chem. Pharm. Bull. 21(2) 241—247 (1973)]

UDC 547.869.057 : 547.551.04 : 547.852.2.04

Studies on the Smiles Rearrangement. XII.[1] Synthesis and Structural Assignment of Two Isomeric N-Phenyl-2,3-diazaphenothiazinones

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(Received March 25, 1972)

Alkaline treatment of 5-(*o*-acetamidophenylthio)-4-chloro-2-phenyl-3(2*H*)-pyridazinone (II) resulted in the exclusive formation of 3-phenyl-10*H*-benzo(*b*)pyridazino-[4,5-*e*][1,4]thiazine-4-(3*H*)-one (III) *via* Smiles rearrangement. Isomeric 2-phenyl-10*H*-benzo[*b*]pyridazino[4,5-*e*][1,4]thiazine-1(2*H*)-one (IV) was obtained preferentially upon treatment of deacetyl derivative (I) with acid together with II. The structures of III and IV were established both by comparison of their chemical properties and by an unequivocal synthesis of IV. A novel ring contraction of IV to spiro(2-phenyl-4(3*H*)-pyrazolone-3,2′-benzothiazoline) (XIV) was observed.

Physiological activities of derivatives of phenothiazine have prompted several groups of workers to synthesize analogues where the benzene rings are replaced by various azaheterocycles.[3] Druey and co-workers[3g] have reported that alkaline treatment of 5-(*o*-acetamidophenylthio)-4-chloro-2-phenyl-3(2*H*)-pyridazinone (II) results in the formation of 2-phenyl-10*H*-benzo[*b*]pyridazino[4,5-*e*][1,4]thiazine-1(2*H*)-one (IV). However, no attention has been paid on the possible formation of isomeric 3-phenyl-10*H*-benzo[*b*]pyridazino[4,5-*e*][1,4]thiazine-4(3*H*)-one (III) *via* the Smiles rearrangement.

In the course of our investigation on the Smiles-type rearrangement employing a number of heterocycles,[1,3a] we had an occasion to examine behavior of 5-(*o*-aminophenylthio)-4-chloro-2-phenyl-3(2*H*)-pyridazinone (I) and its acetate (II) against acid and alkali. It was proved that contrary to Druey's result, alkaline treatment of II yields exclusively III *via* the Smiles rearrangement and IV is obtained upon treatment of I with acid.

The structures of III and IV were established both by comparison of their chemical reactivities and by an unequivocal synthesis of IV. We also found that IV undergoes a novel ring contraction leading to spiro(2-phenyl-4(3*H*)-pyrazolone-3,2′-benzothiazoline) (XIV).

When a suspension of II in 10% aqueous sodium hydroxide was heated at reflux for 2 hr, a red product, III, mp 330° (decomp.), was obtained in excellent yield. The product was identical in every respect with a sample prepared by Druey's procedure (heating in NaOH–dioxane at 125°). On the other hand, treatment of I with a mixture of acetic acid and hydro-

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3) *a*) T. Takahashi and Y. Maki, *Chem. Pharm. Bull.* (Tokyo), **6**, 369 (1958) and preceding papers; *b*) O.R. Rodig, R.E. Collier, and R.K. Schlatzer, *J. Med. Chem.*, **9**, 116 (1966); *c*) W.A. Schuler and H. Kolbe, *Ann.*, **653**, 172 (1962); *d*) H.L. Yale and F. Sowinski, *J. Am. Chem. Soc.*, **80**, 1651 (1958); *e*) P.N. Craig, M. Gordon, Jr., J. Lafferty, M. Payloff, B. Lester, and J.N. Strelitz, *J. Org. Chem.*, **25**, 944 (1960); *f*) A.P. Phillips, N.B. Mehta, and J.N. Strelitz, *J. Org. Chem.*, **28**, 1488 (1963); *g*) J. Druey, *Angew. Chem.*, **70**, 5 (1958); J. Druey, K. Meier, and A. Staehelin, Swiss Patent 382749 (1964); *h*) F. Yoneda and T. Otaka, *Yakugaku Zasshi*, **88**, 1638 (1968) and preceding papers; *i*) D.S. Wise and R. Castle, Abstracts of Papers, Third International Congress of Heterocyclic Chemistry, Sendai, August, 1971, p. 407.

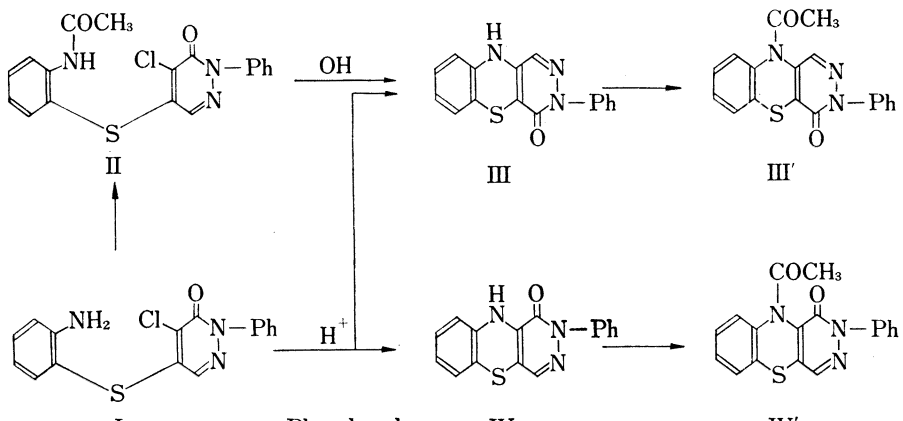

Chart 1

Table I. Some Physical Properties of Two Isomeric N-Phenyl-2,3-diazaphenothiazinones and Their Acetates

Compound	mp (°C)	IR (nujol) cm^{-1}	NMR ($CDCl_3$)τ	UV λ_{max}^{EtOH} mμ (log ε)
III	330 (decomp.)	1325, 3180 (NH) 1630 (C=O)		
III′	193	1680 (CH_3CO)	7.73 (CH_3CO) 1.88 (C_1-H)	225 (3.50) 263 (sh, 3.15) 313 (2.97)
IV	232	3255 (NH) 1628 (C=O)		
IV′	173	1700 (CH_3CO)	7.71 (CH_3CO) 2.12 (C_4-H)	220 (3.43) 250 (sh, 2.98) 322 (2.89)

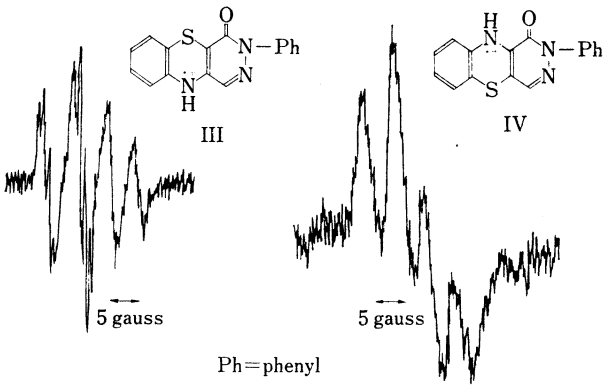

Fig. 1. ESR Spectra of Two Isomeric N-Phenyl-2,3-diazaphenothiazine (III and IV) in conc. Sulfuric Acid

chloric acid at reflux for 20 hr[4] led to the formation of an orange product, IV, mp 232°, and III in the ratio of 6:4. Separation of both products, III and IV, was achieved owing to their different solubilities in chloroform (IV is much more soluble). Interconversion between III and IV was not observed upon treatment with boiling acetic acid-hydrochloric acid mixture. Acetylation of III and IV using acetic anhydride gave their acetates III′ and IV′.

Some physical properties of III, IV, and their acetates are listed in Table I.

4) Yoneda and co-workers have employed this procedure for the cyclization of 5-(*o*-aminophenylthio)-4-chloro-3(2*H*)-pyridazinone to 2,3-diazaphenothiazinone (*cf.* reference 3*h*)).

Addition of III to conc. sulfuric acid gave a green solution which changed to reddish violet on standing. In the case of IV, a stable violet solution was obtained immediately. The electron spin resonance (ESR) spectra of the solutions of III and IV showed signals suggesting the presence of radical cations (*cf.* Fig. 1).

Above spectral data did not allow us unambigous assignment for structures III and IV. The following experiments, however, provide chemical evidence in support of their structures.

An attempt to isolate a rearranged intermediate in the reaction of II with alkali was made: Refluxing of II with methyl iodide in ethanolic sodium ethoxide resulted in the formation of 4-chloro-5-(*o*-methylthioacetanilino)-2-phenyl-3(2*H*)-pyridazinone (V). Structure V was fully supported by the presence of signals due to a methylthio group and an acetyl group in its nuclear magnetic resonance (NMR) spectrum. V underwent easily acid-catalyzed hydrolysis to afford 4-chloro-5-(*o*-methylthioanilino)-2-phenyl-3(2*H*)-pyridazinone (VI). Thus, occurrence of the base-catalyzed Smiles rearrangement of II leaves no doubt and suggests the formation of III rather than IV in the reaction of II with aqueous sodium hydroxide.

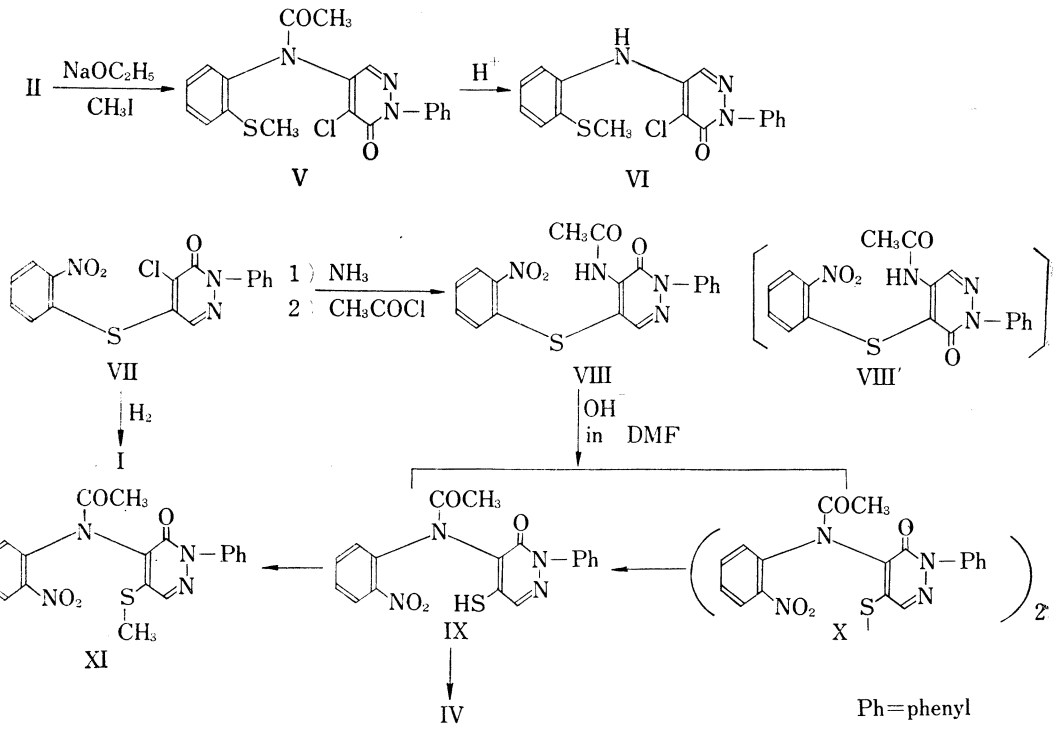

Chart 2

An unequivocal synthesis of IV was achieved as shown in Chart 2: 4-chloro-5-(*o*-nitrophenylthio)-2-phenyl-3(2*H*)-pyridazinone (VII), which can be converted to I by catalytic reduction over paladium-carbon, gave readily 4-acetamide-5-(*o*-nitrophenylthio)-2-phenyl-3(2*H*)-pyridazinone (VIII) upon treatment with ammonia followed by acetylation. Previously, we have observed an anomalous displacement in the reaction of 4-chloro-5-methylthio-2-phenyl-3(2*H*)-pyridazinone with sodium alkoxides, which leads to 5-alkoxy-4-methylthio-2-phenyl-3(2*H*)-pyridazinone.[5] Such unusual reaction, however, did not observe upon employment of aliphatic and aromatic amines instead of sodium alkoxides. Accordingly,

5) Y. Maki and M. Takaya, *Chem. Pharm. Bull.* (Tokyo), **19**, 1635 (1971).

the formation of an alternate 5-acetamido-4-(*o*-nitroacetanilino)-2-phenyl-3(2*H*)-pyridazinone (VIII') in amination of VII can be excluded. Heating of VIII in dimethyl formamide (DMF) containing potassium hydroxide gave 5-mercapto-4-(*o*-nitroacetanilino)-2-phenyl-3(2*H*)-pyridazinone (IX) and its disulfide (X). IX was characterized on the basis of conversion to its methylthio derivative (XI) by action of methyl iodide and its formation from disulfide (X) by the mild alkaline treatment. Further reaction of IX with boiling DMF in the presence of potassium hydroxide resulted in the cyclization to IV. The compound IV thus obtained is identical in every respect with a sample prepared from I as described previously. As a consequence, the structure of III was also established.

A sharp contrast in the chemical behavior between III and IV towerd sodium alkoxide was realized and reflects well their structural differences.

The reaction of III with boiling sodium alkoxide gave sodium salt, whose methylation led to N-methyl derivative (XII). The presence of such an acidic amino group is compatible with structure III which contains a vinylogous amide moiety. After acidification of the alkaline solution, dimer (XIII) was isolated. Structure XIII was supported by its infrared (IR) (no NH bands) and mass (M^+ 584) spectra.

On the other hand, when IV was treated with boiling sodium alkoxide, a remarkable ring contraction was observed.

Refluxing of IV with ethanolic sodium alkoxide for 12 hr, followed by chromatographic separation, afforded a crystalline product, mp 200°, 45% yield. Microanalytical and mass spectral data on the product established the molecular formula $C_{15}H_{11}ON_3S$, indicating a loss of a carbon atom from the parent compound IV. The presence of an NH group in the product was confirmed by spectral data (NMR: $-2.08\,\tau$, deuterium exchangeable; IR: 3200 cm^{-1}), and by conversion to a monoacetate, mp 235°, and a methyl derivative, mp 160°. Furthermore, the NMR spectrum of the product exhibited a highly deshielded signal (1H, singlet, $1.44\,\tau$) other than aromatic proton signals (9H, multiplet, 1.9—3.3 τ). The former signal can attributed to an azomethine proton adjacent to a carbonyl group (C=C–CH=N–).

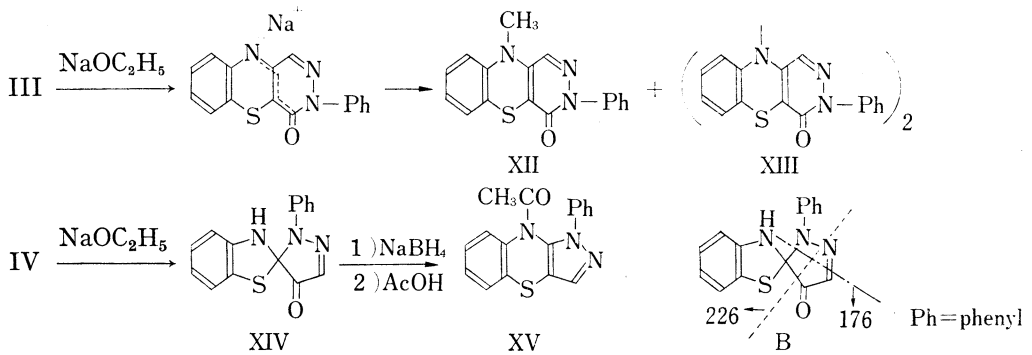

Chart 3

In the ultraviolet (UV) spectrum of the product (λ_{max}^{EtOH} mμ (log ε): 230(sh, 4.13), 257(4.05), 313(3.98), 431(4.39)), three bands in the short wavelength are consistent with those of 2,2-dimethylbenzothiazoline (λ_{max}^{EtOH} mμ (log ε): 231(4.36), 256(sh, 4.69), 312(3.89)), and an absorption band at 431 mμ may be ascribed to a chromophore C_6H_5–N–N=CH–C=O.[6] The above data allow us to assign only a novel spiro-structure XIV to the product. Fragmentation in its mass spectrum is also parallel to structure XIV (*cf.* B).

6) No exactly comparable data are available. We must take into considerations the unique feature of structure XIV in order to account for the ultraviolet (UV) absorption band at 431 mμ. Attempts to clarlify this problem are now in progress.

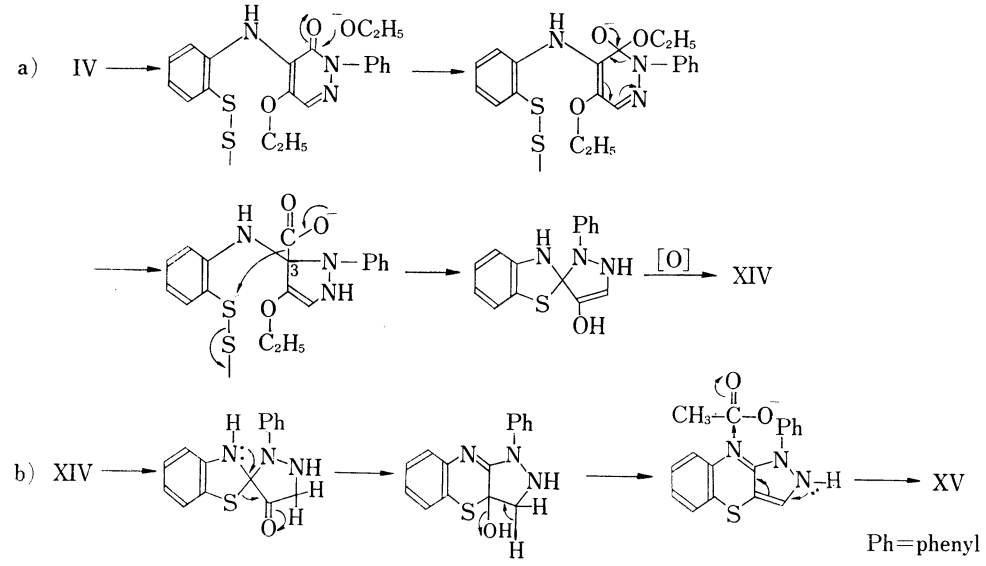

Chart 4

Formation of XIV may be explicable in terms of the mechanism outlined as shown in Chart 4a).

The lability of a C_5-alkylthio group in the 2-phenyl-3(2*H*)pyridazinone system toward nucleophilic displacement[5] has been adequately demonstrated. The reaction seems to involve the ring contraction to pyrazole carboxylic acid,[5,7] nucleophilic attack of an intermediary C_3-carbanion formed *via* decarboxylation on a disulfide linkage and autooxidation.

In the case of III, the initially formed N-anion is stabilized by a conjugated ketonic function and preclude the further attack at position 4 by alkoxide.

Upon sodium borohydride reduction followed by treatment with acetic acid, XIV gave a product, mp 135°, in 50% yield. The structure of 9-acetyl-1-phenylbenzo[*b*]pyrazolo-(4,5-*e*)(1,4)thiazine (XV) was assigned for the product on the basis of the following data: Microanalytical and mass spectral data established the molecular formula $C_{17}H_{13}ON_3S$. Its UV spectrum (λ_{max}^{EtOH} mμ (log ε): 224(4.17), 274(4.24), 332(3.79), 415 (3.43)) indicates a marked skeletal change of the parent compound to a more conjugated system. The presence of an acetyl group in the product was confirmed by its NMR (6.32 τ), IR (1640 cm^{-1}) and mass (M^+ −43) spectra.

We tentatively propose a conceivable mechanism for the formation of XV as shown in Chart 4b). This type of molecular rearrangement[8] is relevant to the unique spiro-structure of XIV.

Further studies on the chemical behavior of this interesting system are now in progress.

Experimental[9]

Reaction of 5-(*o*-Acetamidophenylthio)-4-chloro-2-phenyl-3(2H)-pyridazinone (II) with 10% NaOH——A suspension of 0.3 g of II in 10 ml of 10% NaOH was heated at 130° for 2 hr. After cooling, insoluble

7) Y. Maki and M. Takaya, *Chem. Pharm. Bull.* (Tokyo), **20**, 747 (1972) and preceding papers.
8) For an example of the rearrangement in the spirothiazoline system, see, A. Takamizawa and S. Matsumoto, *Tetrahedron Letters*, 2875 (1969) and preceding papers.
9) All melting points are uncorrected. NMR spectra were measured by a Hitachi Model R-20B instrument at 60 Mc and tetramethylsilane was used as internal standard. Signal multiplicities were represented by s(singlet) and m(multiplet).

substance was collected by filtration, washed well with H_2O and recrystallized from DMF to give 0.2 g of 3-phenyl-10*H*-benzo[*b*]pyridazino-[4,5-*e*][1,4]thiazine-4(3*H*)-one (III) as red prisms, mp 330 (decomp.). *Anal.* Calcd. for $C_{16}H_{11}ON_3S$: C, 65.50; H, 3.78; N, 14.32. Found: C, 65.66; H, 3.97; N, 14.26. This compound was identical in every respect with a sample prepared by the method of Druey.[3g]

Its acetate (III′) was obtained as follows: a solution of 0.2 g of III in Ac_2O was refluxed for 40 hr and concentrated under reduced pressure. The residue was washed with H_2O and recrystallized from MeOH to give 0.08 g of III′ as colorless needles, mp 192—193°. *Anal.* Calcd. for $C_{18}H_{13}O_2N_3S$: C, 64.46; H, 3.90; N, 12.53. Found: C, 64.28; H, 4.14; N, 12.25. The spectral data of III and III′ are listed in Table 1.

Reaction of 5-(*o*-Aminophenylthio)-4-chloro-2-phenyl-3(2H)-pyridazinone (I) with HCl——A solution of 2.0 g of I in a mixture of 10 ml of conc. HCl and 40 ml of AcOH was refluxed for 20 hr. After cooling, the resulting precipitate was collected, washed well with H_2O and taken up with $CHCl_3$. The insoluble substance was recrystallized from DMF to give 0.4 g of III as red prisms, mp 330° (decomp.). III was identical in IR and NMR spectra with a sample obtained in the experiment described above.

The $CHCl_3$ solution was concentrated and the resulting residue was recrystallized from MeOH to give 0.6 g of 2-phenyl-10*H*-benzo[*b*]pyridazino-[4,5-*e*][1,4]thiazine-1(2*H*)-one (IV) as red needles, mp 232—233°. *Anal.* Calcd. for $C_{16}H_{11}ON_3S$: C, 65.50; H, 3.78; N, 14.32. Found: C, 65.49; H, 3.92; N, 14.14. A similar treatment of 0.2 g of IV with Ac_2O as in the case of III gave 0.05 g of its acetate (IV′) as light yellow needles (from EtOH), mp 173—174°. *Anal.* Calcd. for $C_{18}H_{13}O_2N_3S$: C, 64.46; H, 3.90; N, 12.53. Found: C, 64.18; H, 3.95; N, 12.24. The spectral data of IV and IV′ are listed in Table I.

Reaction of II with 5% NaOH in the Presence of CH_3I——To a solution of 1.0 g of II and 2.0 g of CH_3I in 100 ml of acetone was added 5 ml of 5% NaOH under refluxing for 10 min and to this further added an excess of CH_3I. The reaction mixture was further heated at reflux for 1 hr and concentrated under reduced pressure. The residue was purified by silica gel chromatography (solvent $CHCl_3$) and recrystallized from ether to give 0.3 g of 4-chloro-5-(*o*-methylthioacetanilino)-2-phenyl-3(2*H*)-pyridazinone (V) as colorless prisms, mp 122—124°. IR (Nujol) cm^{-1}: 1695, 1660 (C=O). NMR (DMSO-d_6) τ: 7.93 (3H, s, OCH_3), 7.42 (3H, s, SCH_3), 2.75—2.10 (9H, m, aromatic protons), 1.98 (1H, s, C_6-H). *Anal.* Calcd. for $C_{19}H_{16}O_2N_3SCl$: C, 59.14; H, 4.18; N, 10.89. Found: C, 59.37; H, 4.24; N, 10.91.

Acid-catalyzed hydrolysis of V gave 4-chloro-5-(*o*-methylthioanilino)-2-phenyl-3(2*H*)-pyridazinone (VI); mp 228—231°, light yellow prisms (from acetone). IR (Nujol) cm^{-1}: 3350 (NH), 1650 (C=O). *Anal.* Calcd. for $C_{17}H_{14}ON_3SCl$: C, 59.38; H, 4.10; N, 12.12. Found: C, 59.11; H, 4.03; N, 12.01.

An Unequivocal Synthesis of IV——a) 4-Chloro-5-(*o*-nitrophenylthio)-2-phenyl-3(2*H*)-pyridazinone (VII): To a solution of 2.4 g of 4,5-dichloro-2-phenyl-3(2*H*)-pyridazinone in 300 ml of MeOH was added a mixture of 1.7 g of *o*-nitrothiophenol and 0.25 g of Na in 40 ml of MeOH at 20° for 15 min. The reaction mixture was stirred at 25° for 1 hr and the precipitated crystalline solid was fractionated by recrystallization from EtOH–acetone (5:1) to give 1.2 g of VII (more soluble) as yellow plates, mp 189—190°, and 0.4 g of 4,5-bis(*o*-nitrophenylthio)-2-phenyl-3(2*H*)-pyridazinone (less soluble) as yellow powder, mp 214—216°. VII: IR (Nujol) cm^{-1}: 1670 (C=O), 1530, 1355 (NO_2). Mass Spectrum *m/e*: 359 (M^+). *Anal.* Calcd. for $C_{16}H_{10}O_3N_3SCl$: C, 53.40; H, 2.78; N, 11.68. Found: C, 53.30; H, 2.71; N, 11.46. 4,5-Bis(*o*-nitrophenylthio)-2-phenyl-3(2*H*)-pyridazinone: IR (Nujol) cm^{-1}: 1670 (C=O), 1520, 1340 (NO_2). *Anal.* Calcd. for $C_{22}H_{14}O_5N_4S_2$: C, 55.23; H, 2.93; N, 11.71. Found: C, 54.58; H, 2.95; N, 11.50.

To a solution of 0.4 g of $SnCl_2$–$2H_2O$ in 4 ml of conc. HCl was added 0.2 g of VII in portions. The reaction mixture was stirred at 65° over a period of 3 hr, cooled, diluted with H_2O, basified with 20% NaOH, and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O and dried over anhyd. Na_2SO_4. After evaporation of the solvent, the residue was recrystallized from EtOH to give 120 mg of I as colorless prisms, mp 151—152°. I thus obtained was identical in every respect with a sample obtained by the reaction of 4,5-dichloro-2-phenyl-3(2*H*)-pyridazinone with *o*-aminothiophenol.

b) 4-Acetamido-5-(*o*-nitrophenylthio)-2-phenyl-3(2*H*)-pyridazinone (VIII)——VII (1.5 g) was heated with 50 ml of 13% NH_3 in EtOH at 100° in a sealed tube for 10 hr. The reaction mixture was concentrated under reduced pressure to dryness. The residue was washed with H_2O, dried, and recrystallized from acetone–MeOH (2:1) to give 1.1 g of 4-amino-5-(*o*-nitrophenylthio)-3(2*H*)-pyridazinone as yellow needles, mp 189—191°. IR (Nujol) cm^{-1}: 3450, 3300 (NH_2), 1650 (C=O), 1520, 1340 (NO_2). *Anal.* Calcd. for $C_{16}H_{12}O_3N_4S$: C, 56.47; H, 3.55; N, 16.47. Found: C, 56.28; H, 3.58; N, 16.63.

4-Amino-5-(*o*-nitrophenylthio)-2-phenyl-3(2*H*)-pyridazinone (0.5 g) was heated with 12 ml of CH_3COCl at 90° for 7 hr. The reaction mixture was concentrated under reduced pressure to dryness and the residue was recrystallized from $CHCl_3$ to give 0.54 g of VIII as yellow prisms, mp 243—245°. IR (Nujol) cm^{-1}: 3260 (NH), 1700, 1630 (C=O), 1515, 1360 (NO_2). *Anal.* Calcd. for $C_{18}H_{14}O_4N_4S$: C, 56.54; H, 3.69; N, 14.66. Found: C, 56.56; H, 3.86; N, 14.53.

c) Reaction of VIII with NaOH——To a solution of 0.25 g of VIII in 7 ml of DMF was added 1 ml of 10% NaOH. The reaction mixture was heated at 160° for 5 min and concentrated under reduced pressure to dryness. The residue was washed with H_2O. A small amount of insoluble substance was recrystallized from acetone to give 0.03 g of disulfide (X) as orange powder, mp 172—177° (decomp.). IR (Nujol) cm^{-1}: 1710 1660 (C=O), 1540, 1350 (NO_2). *Anal.* Calcd. for $C_{36}H_{26}O_8N_8S_2$: C, 56.65; H, 3.41; N, 14.68. Found: C, 56.82; H, 3.30; N, 14.48. The alkaline washings were acidified with 10% HCl and allowed to stand at

room temperature overnight. The precipitated solid was collected and washed with H_2O to give 0.19 g of IX as orange powder, mp 115—135° (decomp.). IR (Nujol) cm^{-1}: 2540 (SH), 1700, 1660 (C=O), 1540, 1360 (NO_2). IX was so unstalbe that its purification by recrystallization resulted in contamination with disulfide X, which is reconverted to IX by the mild alkaline treatment (heating in 2% NaOH at 60° for 15 min). IX was characterized as its methylthio derivative XI: To a solution of 0.1 g of IX in methanolic sodium methoxide (0.01 g of Na metal in 1 ml of MeOH) was added 0.06 ml of CH_3I. After being allowed to stand for 1 hr, the reaction mixture was concentrated under reduced pressure. The residue was washed with H_2O and recrystallized from acetone to give 0.05 g of XI as orange needles, mp 189—191°. IR (Nujol) cm^{-1}: 1660, 1650 (C=O), 1510, 1360 (NO_2). *Anal.* Calcd. for $C_{19}H_{16}O_4N_4S$: C, 57.57; H, 4.07; N, 14.14. Found: C, 57.66; H, 3.90; N, 15.06.

d) Reaction of IX with NaOH——IX (0.16 g) was heated in a mixture of DMF (5 ml) and 10% NaOH (1.5 ml) at 110° for 1 hr. The reaction mixture was concentrated under reduced pressure and diluted with H_2O. The deposited crystals were recrystallized from EtOH to give 0.02 g of IV as red needles, mp 236°, identical in IR and NMR spectra with a sample obtained by the acid treatment of I.

Reaction of III with Sodium Ethoxide in the Presence of CH_3I——To a solution of 0.4 g of Na metal in 40 ml of EtOH was added 0.3 g of III. The reaction mixture was refluxed for 20 min and to this added 4 ml of CH_3I. The reaction mixture was further refluxed for 20 min and concentrated under reduced pressure. The residue was washed with H_2O and recrystallized from MeOH to give 0.1 g of 10-methyl-3-phenyl-10*H*-benzo[*b*]pyridazino[4,5-*e*]-thiazine-4(3*H*)-one (XII) as orange needles, mp 208—209°. IR (Nujol) cm^{-1}: 1640 (sh), 1630 (C=O). UV λ_{max}^{EtOH} mμ (log ε): 234 (sh, 4.07), 275 (4.51), 316 (3.92), 433 (3.08). NMR (DMSO-d_6) τ: 6.67 (3H, s, NCH_3), 3.4—2.3 (4H, m, aromatic protons), 2.51 (5H, s, C_6H_5), 2.06 (1H, s, C_1-H). *Anal.* Calcd. for $C_{17}H_{13}ON_3S$: C, 66.42; H, 4.26; N, 13.67. Found: C, 66.17; H, 4.17; N, 13.84. The alkaline washings were acidified with dil. HCl. The resulting precipitate was collected by filteration, washed with H_2O and recrystallized from EtOH to give 0.07 g of dimer (XIII) as colorless prisms, mp 271° (decomp.). IR (Nujol) cm^{-1}: 1650 (C=O). NMR (DMSO-d_6)τ: 1.78 (2H, s, C_1-H×2), 2.47 (10H, s, C_6H_5×2), 1.85—2.80 (8H, m, aromatic protons). Mass Spectrum *m/e*: 584 (M^+), 292. *Anal.* Calcd. for $C_{32}H_{20}O_2N_6S_2 \cdot 2H_2O$: C, 61.92; H, 3.90; N, 13.54. Found: C, 61.70; H, 3.70; N, 13.54.

Reaction of IV with Sodium Ethoxide——To a solution of 0.4 g of Na metal in 40 ml of EtOH was added 0.3 g of IV. The reaction mixture was refluxed for 12 hr and concentrated under reduced pressure. The resulting residue was neutralized with dil. HCl and extracted with $CHCl_3$. The $CHCl_3$ extract was chromatographed on silica gel (solvent $CHCl_3$). The first effluent was recrystallized from MeOH to give 0.13 g of spiro(2-phenyl-4(3*H*)-pyrazolone-3,2′-benzothiazoline)(XIV) as red needles, mp 199—200°. IR (Nujol) cm^{-1}: 3200 (NH), 1620 (C=O). UV λ_{max}^{EtOH} mμ (log ε): 230 (sh, 4.13), 257 (4.05), 313 (3.98), 431 (4.39). Mass Spectrum *m/e*: 281 (M^+), 226 (base peak), 176, 148. NMR (DMSO-d_6)τ: 3.3—1.9 (9H, m, aromatic protons), 1.44 (1H, s, C_3-H in pyrazole ring). *Anal.* Calcd. for $C_{15}H_{11}ON_3S$: C, 64.03; H, 3.94; N, 14.94. Found: C, 64.01; H, 4.10; N, 14.95.

From the second elute 0.05 g of unchanged IV was recovered.

Monoacetate of XIV was obtained by the reaction of 0.25 g of XIV with 2 ml of Ac_2O in 5 ml of pyridine at room temperature: mp 234—235°, pale yellow needles (from MeOH), yield 0.15 g. IR (Nujol) cm^{-1}: 1700, 1670 (C=O). UV λ_{max}^{EtOH} mμ (log ε): 224 (sh, 4.34), 246 (sh, 3.96), 316 (4.04). NMR ($CDCl_3$)τ: 7.27 (3H, s, $COCH_3$), 2.30 (1H, s, C_3-H in pyrazole ring). *Anal.* Calcd. for $C_{17}H_{13}O_2N_3S$: C, 63.14; H, 4.05; N, 12.00. Found: C, 63.16; H, 4.26; N, 13.21.

Monomethylate of XIV was prepared by the reaction of 0.2 g of XIV with ethanolic sodium ethoxide (0.4 g of Na metal in 40 ml of EtOH) in the presence of 5 ml of CH_3I under refluxing: mp 159—160°, orange needles (from MeOH), yield 0.1 g. IR (Nujol) cm^{-1}: 1640 (C=O). UV λ_{max}^{EtOH} mμ (log ε): 226 (sh, 4.20), 257 (4.10), 309 (3.98), 400 (4.35). NMR (DMSO-d_6)τ: 6.56 (3H, s, NCH_3), 1.90 (1H, s, C_3-H in pyrazole ring). *Anal.* Calcd. for $C_{16}H_{13}ON_3S$: C, 65.06; H, 4.42; N, 14.23. Found: C, 65.43; H 4.56; N, 14.26.

Reaction of XIV with $NaBH_4$——A mixture of 0.1 g of XIV and 0.1 g of $NaBH_4$ in 20 ml of THF was allowed to stand overnight under stirring. An excess of $NaBH_4$ was decomposed with 80% AcOH and the reaction mixture was concentrated under reduced pressure. The residue was washed with H_2O and recrystallized from petroleum ether (bp 30—70°) to give 0.05 g of 9-acetyl-1-phenylbenzo[*b*]pyrazolo[4,5-*e*][1,4]-thiazine (XV) as light yellow needles, mp 135°. IR (nujol) cm^{-1}: 1640 (C=O). UV λ_{max}^{EtOH} mμ (log ε): 224 (sh, 4.17), 274 (4.24), 332 (sh, 3.79), 415 (3.43). Mass Spectrum *m/e*: 307 (M^+, base peak), 292 (M-CH_3), 274 (M-$COCH_3$). NMR ($CDCl_3$)τ: 6.32 (3H, s, $COCH_3$), 2.4—3.2 (10H, m, aromatic protons). *Anal.* Calcd. for $C_{17}H_{13}ON_3S$: C, 66.42; H, 4.26; N, 13.67. Found: C, 66.59; H, 4.56; N, 13.40.