

[Chem. Pharm. Bull.]
25(12)3270-3276(1977)

UDC 547.789.6'546.21.04 : 547.292-931.04

Studies on Azole Compounds. IV.¹⁾ Reaction of 2,5-Diarylthiazole
3-Oxides with Acetic Anhydride. Isolation of the Intermediates,
4,5-Diacetoxy-2,5-diaryl-4,5-dihydrothiazoles

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(Received April 28, 1977)

The reaction of 2,5-diarylthiazole 3-oxides (IIa—e) with acetic anhydride was studied. The intermediates of this reaction, 4,5-diacetoxy-2,5-diaryl-4,5-dihydrothiazoles (Va-1—Ve-1, Va-2—Ve-2), were isolated and their structures were determined by their chemical behavior and spectral data.

Keywords—2,5-diarylthiazole 3-oxides; 4,5-dihydrothiazoles; rearrangement reaction of N-oxide; mass; NMR

In the previous paper,¹⁾ it has been shown that the methyl group of the 4-position of 4,5-dimethyl-2-aryloxazole 3-oxides were attacked by acetoxy group to give 4-acetoxymethyl-oxazole derivatives. When the thiazole has the methyl group on the 2-position of the ring, the 2-methyl group of the N-oxides is predominantly attacked by acetoxy group than the 4-methyl group. Rearrangements to form a thiazole with an acetoxy group in an open 2- or 5-position also take place with these thiazole derivatives³⁾ (Chart 1).

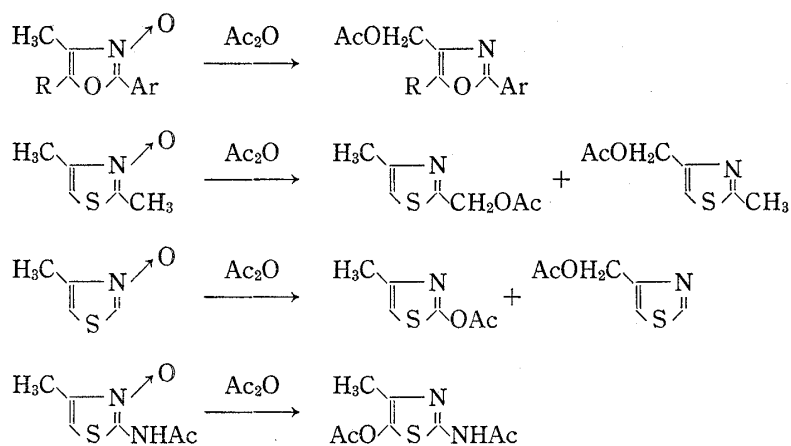


Chart 1

The present investigation was carried out to examine the reaction of 2,5-diarylthiazole 3-oxides, which have no substituent on the 4-position, with acetic anhydride. These thiazole N-oxides (IIa—e) were prepared by the oxidation reaction of the corresponding thiazoles (Ia—e) with maleic anhydride and hydrogen peroxide.⁴⁾ The results obtained are shown in

1) Part III: Y. Goto, M. Yamazaki, and M. Hamana, *Chem. Pharm. Bull.* (Tokyo), **19**, 2050 (1971).

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3) a) H.J. Anderson, D.J. Barnes, and Z.M. Khan, *Can. J. Chem.*, **42**, 2375 (1964); b) K. Arakawa, T. Miyasaka, and K. Arata, Abstracts of Papers, 89th Annual Meeting of the Pharmaceutical Society of Japan, Nagoya, April, 1969, p. 249.

4) M. Yamazaki, N. Honjo, K. Noda, Y. Chono, and M. Hamana, *Yakugaku Zasshi*, **86**, 749 (1966).

Table I. All the compounds have a strong absorption band around 1210 cm^{-1} indicative of an aromatic N-oxide group in infrared (IR) spectra. The ultraviolet (UV) absorption spectra showed the hypsochromic shift in protic solvents compared with those in aprotic solvents, which observation is generally noticed as one of the characteristics of aromatic N-oxides; a typical example is shown in Figure 1. These compounds afforded the corresponding deoxygenated thiazole derivatives by the reaction with phosphorus trichloride. These spectral and chemical properties indicate that these compounds have an N-oxide group.

TABLE I. 2,5-Diarylthiazole 3-Oxides

$\text{Ar}_1-\text{C}=\text{N}-\text{C}=\text{Ar}_2 \xrightarrow[\text{H}_2\text{O}_2]{\text{maleic anhydride}} \text{Ar}_1-\text{C}=\text{N}(\text{O})-\text{C}=\text{Ar}_2$				
	Ar ₁	Ar ₂	II	
			mp (°C)	Yield (%)
a	C ₆ H ₅	C ₆ H ₅	147—148	44
b	C ₆ H ₅	<i>o</i> -ClC ₆ H ₄	165—166	52
c	C ₆ H ₅	<i>p</i> -ClC ₆ H ₄	182—183	52
d	<i>p</i> -CH ₃ C ₆ H ₄	C ₆ H ₅	180	40
e	<i>p</i> -CH ₃ C ₆ H ₄	<i>p</i> -ClC ₆ H ₄	193—194	41

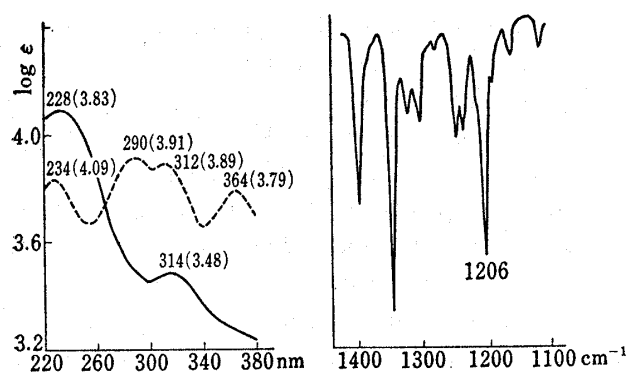
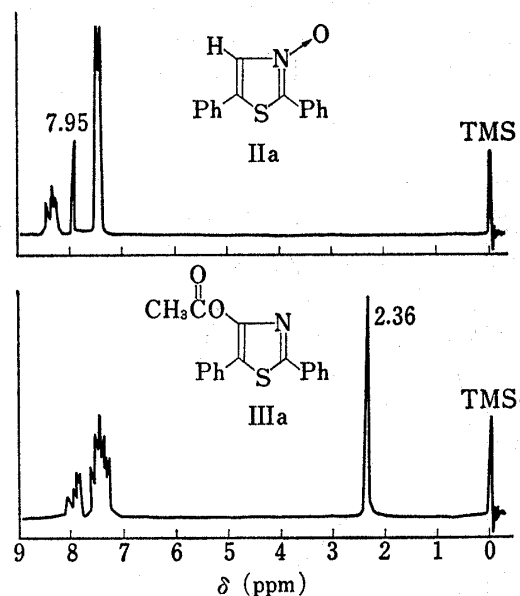


Fig. 1. UV Spectra (solvent: — EtOH, ---- Dioxane) and IR Spectrum (KBr) of IIa

Fig. 2. NMR Spectra of IIa and IIIa (in CDCl₃, 60 MHz, TMS)

A solution of 2,5-diphenylthiazole 3-oxide (IIa) in acetic anhydride was heated at 130° for 3 hours. From the reaction mixture, a crystalline substance C₁₇H₁₃NO₂S (IIIa) was obtained in 95% yield. The ¹H nuclear magnetic resonance (¹H NMR) spectra of the starting N-oxide (IIa) and its rearrangement product (IIIa) are shown in Figure 2. As shown in Figure 2, the characteristic resonance line at δ 7.95 ppm disappeared, which is due to the presence of proton on the 4-position of thiazole ring, and the new acetoxy proton resonance at δ 2.36 ppm appeared.

A suspension of IIIa in 10% hydrochloric acid was refluxed for 10 hours to afford 4-hydroxy-2,5-diphenylthiazole (IVa) which was identified by comparison of its infrared spectrum with that of an authentic sample.⁵⁾ The structure of IIIa was then unanimously determined as 4-acetoxy-2,5-diphenylthiazole. The results obtained are shown in Table II.

TABLE II. Reactions of IIa—e with Ac₂O and Hydrolysis of IIIa—e

$ \begin{array}{ccccc} \text{Ar}_1 \text{---} \text{C} \text{---} \text{N} \text{---} \text{O} & \xrightarrow{\text{Ac}_2\text{O}} & \text{AcO} \text{---} \text{C} \text{---} \text{N} & \xrightarrow{\text{HCl}} & \text{HO} \text{---} \text{C} \text{---} \text{N} \\ \parallel & & \parallel & & \parallel \\ \text{S} & & \text{S} & & \text{S} \\ \text{II} & & \text{III} & & \text{IV} \end{array} $						
	Ar ₁	Ar ₂	III		IV	
			mp(°C)	Yield(%)	mp(°C)	Yield(%)
a	C ₆ H ₅	C ₆ H ₅	105	95	210—211.5	73
b	C ₆ H ₅	<i>o</i> -ClC ₆ H ₄	108—109	86	209—211	69
c	C ₆ H ₅	<i>p</i> -ClC ₆ H ₄	147—148	95	245—246	83
d	<i>p</i> -CH ₃ C ₆ H ₄	C ₆ H ₅	161—163	98	227	70
e	<i>p</i> -CH ₃ C ₆ H ₄	<i>p</i> -ClC ₆ H ₄	143	86	263—265	65

On the other hand, a solution of 2,5-diphenylthiazole 1-oxide (IIa) in acetic anhydride was heated at 100° for 2 hours. Besides the compound IIIa, two kinds of crystalline substances C₁₉H₁₇NO₄S (Va-1) and C₁₉H₁₇NO₄S (Va-2) were isolated from the reaction mixture. Both Va-1 and Va-2 were converted into IIIa by further heating of these compounds in acetic anhydride at 130° for 3 hours. The isolation of IIIa showed that no skeletal transformation of IIa occurred. The UV and mass spectra of Va-1 and Va-2 are identical.

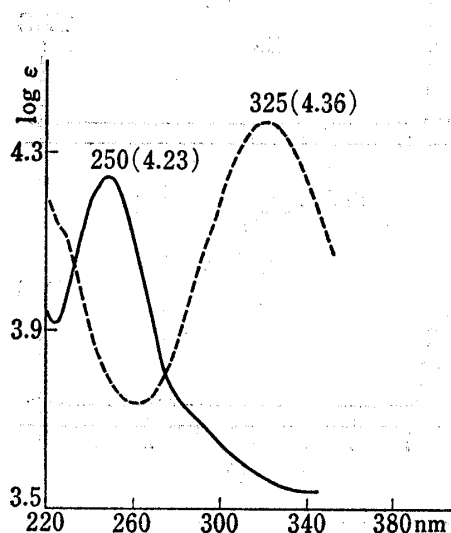
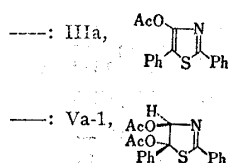


Fig. 3. UV Spectra of IIIa and Va-1 in EtOH



As shown in Figure 3, no absorption due to a phenylthiazole ring in the UV spectrum of Va-1 shows that Va-1 seems to be a structure having a dihydrothiazole ring.

The mass spectra of IIIa, Va-1 and Va-2 are shown in Figure 4. The mass spectrum of IIIa showed peaks at the following positions, *m/e* 295 (molecular ion), 253, 150, 121 and 104. The *m/e* 253 was formed by the loss of ketene from the molecular ion (metastable peak at *m/e* 217.0), and furthermore the *m/e* 150 should come from the *m/e* 253 ion from which benzonitrile was eliminated (metastable peak at *m/e* 88.9). The fragment ions at *m/e* 121 and 104 are assumed as C₆H₅C=S⁺ and C₆H₅C=NH⁺ respectively. The spectrum of Va-1 shows that the *m/e* 295 was produced by the elimination of acetic acid from the molecular ion, and the peak at *m/e* 105 was observed except for the *m/e* 121 and 104. The *m/e* 105 is regarded as the fragment ion C₆H₅C=O⁺ shown in Figure 4. As Figure 4 and Table III show, all the peaks

5) E.C. Taylor, Jr., J.A. Anderson, and G.A. Berchtold, *J. Am. Chem. Soc.*, **77**, 5444 (1955).

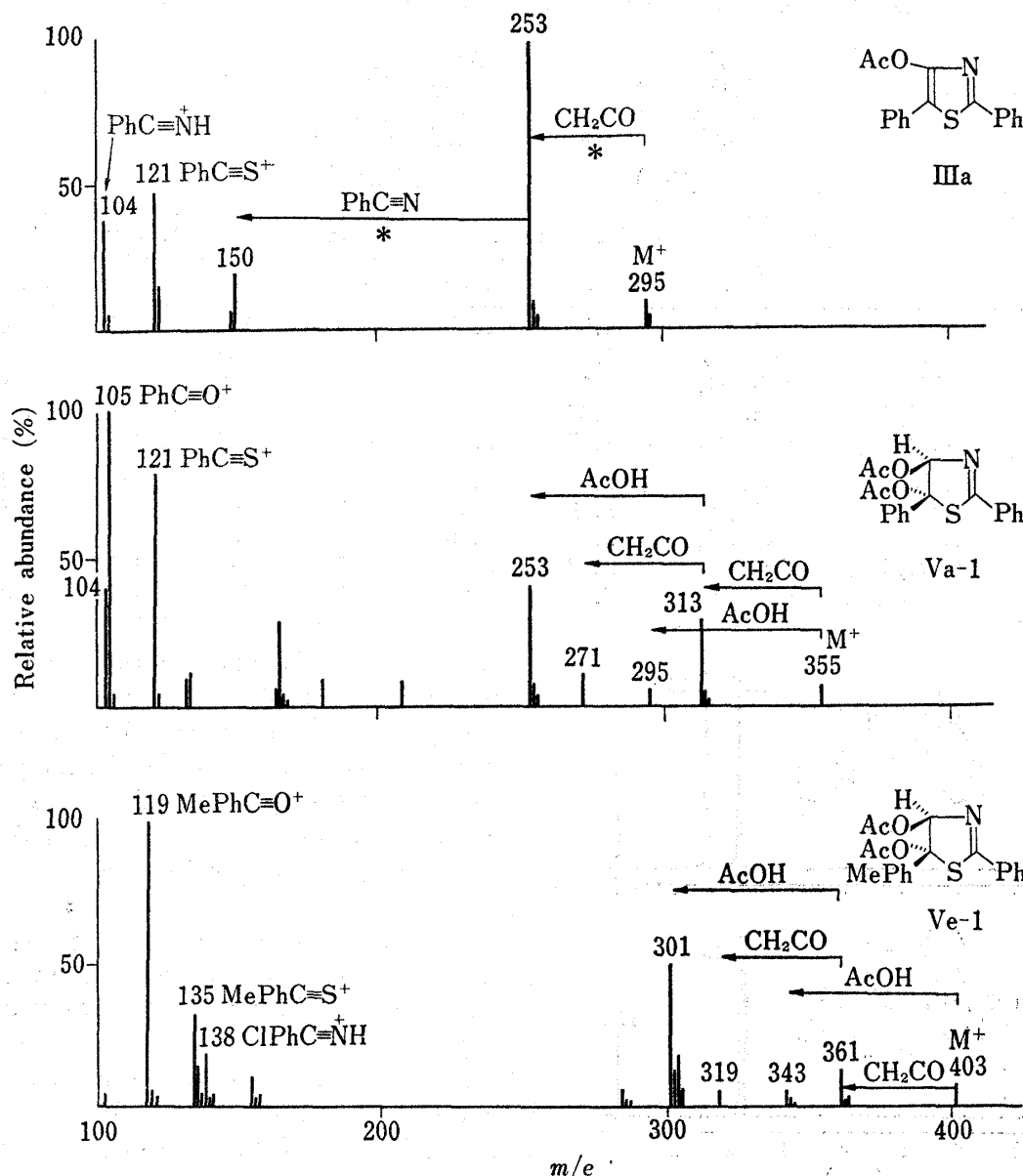


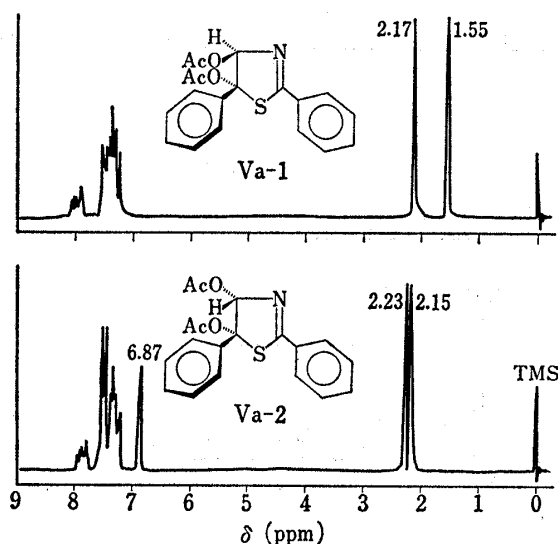
Fig. 4. Mass Spectra of IIIa, Va-1 and Ve-1

of the mass spectrum of Ve-1 correspond to those of the spectrum of Va-1. In the spectrum of Ve-1, no peak corresponding to the ion $\text{ClC}_6\text{H}_4\text{C}=\text{O}^+$ was observed. From the above results of the mass spectra and the formation of IIIa—e in the heating of Va-1—Ve-1 in acetic anhydride, it is concluded that two acetoxy groups entered the 4- and 5-position of the thiazole ring respectively. In conclusion, the planar structures of dihydrothiazoles were determined to be 4,5-diacetoxy-4,5-dihydrothiazoles.

The ^1H NMR spectra of Va-1 and Va-2 are given in Figure 5. The spectrum of Va-1 shows the two peaks due to the methyl protons of the two acetoxy groups as a singlet at δ 1.55 (3H) and 2.17 (3H) respectively. On the other hand, two signals due to the methyl protons of the two acetoxy groups in the spectrum of Va-2 appear at δ 2.15 (3H) and 2.23 (3H) respectively. In the spectrum of Va-2 the peak at δ 6.87 (1H) is ascribed to the proton on the 4-position of the dihydrothiazole ring. The signal of the proton on the 4-position in the spectrum of Va-1 is regarded as falling within the complex multiplets arising from the aromatic protons δ 7.15—7.65. From the results described above, it is considered that the

TABLE III. ^1H NMR and Mass Spectra of Va-1—Ve-1 and Va-2—Ve-2

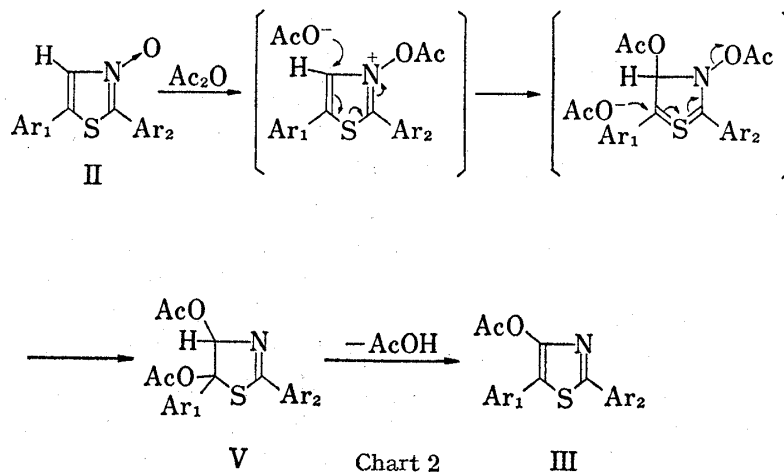
	Ar_1	Ar_2	^1H NMR δ in CDCl_3 , 60 MHz			Mass (m/e)		
			4- CH_3CO_2	5- CH_3CO_2	4-H	$\text{Ar}_1\text{C}\equiv\text{O}^+$	$\text{Ar}_1\text{C}\equiv\text{S}^+$	$\text{Ar}_2\text{C}\equiv\text{NH}^+$
V-1a	C_6H_5	C_6H_5	1.55	2.17	—	105	121	104
b	C_6H_5	<i>o</i> - ClC_6H_4	1.53	2.13	—	105	121	138
c	C_6H_5	<i>p</i> - ClC_6H_4	1.53	2.15	—	105	121	138
d	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	C_6H_5	1.56	2.16	—	119	135	104
e	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	<i>p</i> - ClC_6H_4	1.57	2.15	—	119	135	138
V-2a	C_6H_5	C_6H_5	2.23	2.15	6.87	105	121	104
b	C_6H_5	<i>o</i> - ClC_6H_4	2.19	2.16	6.74	105	121	138
c	C_6H_5	<i>p</i> - ClC_6H_4	2.22	2.15	6.75	105	121	138
d	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	C_6H_5	2.23	2.14	6.77	119	135	104
e	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	<i>p</i> - ClC_6H_4	2.23	2.16	6.79	119	135	138

Fig. 5. NMR Spectra of Va-1 and Va-2 (in CDCl_3 , 60 MHz, TMS)

signal at δ 1.55 (3H) in the spectrum of Va-1 appear at higher field by the anisotropic effect of the phenyl group on the 5-position than that in the spectrum of Va-2, while the peak at δ 6.87 (1H) in the spectrum of Va-2 is shifted at higher field by the same effect indicated above than the corresponding peak in that of Va-1.

It is therefore concluded that the compound Va-1 has the *trans*-form, while the Va-2 has the *cis*-form in terms of acetoxy groups (Figure 5).

The compound Va-1 was easily converted into IIIa by pyrolysis at 160° for 15 minutes, while in the case of Va-2 no change occurred under the same condition. The results of this pyrolysis also clearly support the proposed structure indicated above.



On the basis of these data above, it is considered that III is formed according to the scheme (Chart 2); addition of the carbonyl group acetic anhydride to the oxygen of thiazole 3-oxide (II), attack by an acetate ion to the 4-position of thiazole ring, attack by another acetate ion at the 5-position and the simultaneous cleavage of the N-O bond giving V, and the elimination of acetic acid from V finally giving III.

Experimental⁶⁾

Preparation of 2,5-Diaryl-thiazole 3-Oxides⁴⁾

General Procedure—To a solution of maleic anhydride (30 g) in CHCl_3 (60 ml) was added dropwise 30% H_2O_2 (12 g) with stirring under ice-cooling. After stirring 2 hr under the same condition, thiazole (0.021 mol) was added and the mixture was stirred for further 1 hr. The resulting mixture was allowed to stand for 5 days in the refrigerator. The reaction mixture was made slightly alkaline with conc. NH_4OH under ice-cooling, extracted with CHCl_3 , the CHCl_3 extract was dried over anhyd. K_2CO_3 and CHCl_3 was removed. The residue was chromatographed over alumina with CHCl_3 , and recrystallized from acetone to give thiazole N-oxides (IIa—e).

2,5-Diphenylthiazole 3-Oxide (IIa)—Colorless fine needles, mp 147—148°, 44% yield. *Anal.* Calcd. for $\text{C}_{15}\text{H}_{11}\text{NOS}$: C, 71.14; H, 4.37; N, 5.53. Found: C, 70.94; H, 4.16; N, 5.49. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1206 (N→O).

2-(o-Chlorophenyl)-5-phenylthiazole 3-Oxide (IIb)—Colorless needles, mp 165—166°, 52% yield. *Anal.* Calcd. for $\text{C}_{15}\text{H}_{10}\text{ClNOS}$: C, 62.60; H, 3.50; N, 4.87. Found: C, 62.78; H, 3.41; N, 4.68. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1209 (N→O).

2-(p-Chlorophenyl)-5-phenylthiazole 3-Oxide (IIc)—Pale yellow scales, mp 182—183°, 52% yield. *Anal.* Calcd. for $\text{C}_{15}\text{H}_{10}\text{ClNOS}$: C, 62.60; H, 3.50; N, 4.87. Found: C, 62.84; H, 3.37; N, 4.59. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1208 (N→O).

2-Phenyl-5-(p-toluy)-thiazole 3-Oxide (IIId)—Pale yellow scales, mp 180°, 40% yield. *Anal.* Calcd. for $\text{C}_{16}\text{H}_{13}\text{NOS}$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.68; H, 4.74; N, 5.47. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1204 (N→O).

2-(p-Chlorophenyl)-5-(p-toluy)-thiazole 3-Oxide (IIe)—Pale yellow scales, mp 193—194°, 41% yield. *Anal.* Calcd. for $\text{C}_{16}\text{H}_{12}\text{ClNOS}$: C, 63.67; H, 4.01; N, 4.64. Found: C, 63.92; H, 4.09; N, 4.43. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1207 (N→O).

Reaction of IIa—e with Acetic Anhydride to give IIIa—e

General Procedure—A solution of IIa—e (1 g) in Ac_2O (2 ml) was heated at 130° under the condition described below respectively. Into the reaction mixture MeOH (5 ml) was added, and the solution was evaporated *in vacuo* to dryness. To the residue was added H_2O (5 ml), neutralized with NaHCO_3 , extracted with CHCl_3 . The CHCl_3 extract was dried over anhyd. Na_2SO_4 , and CHCl_3 was removed. The residue was recrystallized to give 4-acetoxy-2,5-diarylthiazoles (IIIa—e).

4-Acetoxy-2,5-diphenylthiazole (IIIa)—Reaction time: 3 hr. Colorless needles (from ether-petr. ether), mp 105°, 95% yield. *Anal.* Calcd. for $\text{C}_{17}\text{H}_{13}\text{NO}_2\text{S}$: C, 69.14; H, 4.44; N, 4.74. Found: C, 69.01; H, 4.31; N, 4.67.

4-Acetoxy-2-(o-chlorophenyl)-5-phenylthiazole (IIIb)—Reaction time: 3 hr. Colorless leaflets (from petr. ether), mp 108—109°, 86% yield. *Anal.* Calcd. for $\text{C}_{17}\text{H}_{12}\text{ClNO}_2\text{S}$: C, 61.91; H, 3.67; N, 4.25. Found: C, 62.19; H, 3.45; N, 4.31.

4-Acetoxy-2-(p-chlorophenyl)-5-phenylthiazole (IIIc)—Reaction time: 4 hr. Colorless columns (from acetone-petr. ether), mp 147—148°, 95% yield. *Anal.* Calcd. for $\text{C}_{17}\text{H}_{12}\text{ClNO}_2\text{S}$: C, 61.91; H, 3.67; N, 4.25. Found: C, 62.08; H, 3.36; N, 4.11.

4-Acetoxy-2-phenyl-5-(p-toluy)-thiazole (IIId)—Reaction time: 3 hr. Colorless needles (from acetone), mp 161—163°, 97% yield. *Anal.* Calcd. for $\text{C}_{18}\text{H}_{15}\text{NO}_2\text{S}$: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.92; H, 4.99; N, 4.67.

4-Acetoxy-2-(p-chlorophenyl)-5-(p-toluy)-thiazole (IIIe)—Reaction time: 4 hr. Colorless needles (from ether), mp 143°, 86% yield. *Anal.* Calcd. for $\text{C}_{18}\text{H}_{14}\text{ClNO}_2\text{S}$: C, 62.88; H, 4.10; N, 4.07. Found: C, 62.84; H, 3.95; N, 4.09.

Hydrolysis of IIIa—e with Hydrochloric Acid

General Procedure—A solution of IIIa—e (0.5 g) in 10 ml of 10% HCl was refluxed for 10 hr. After cooling the precipitated crystals were filtered, washed with water, recrystallized to afford IVa—e.

4-Hydroxy-2,5-diphenylthiazole (IVa)—Yellow needles (from acetone), mp 210—211.5°, 73% yield. *Anal.* Calcd. for $\text{C}_{15}\text{H}_{11}\text{NOS}$: C, 71.14; H, 4.37; N, 5.53. Found: C, 71.28; H, 4.41; N, 5.67.

6) All melting points are uncorrected. UV spectra were measured on a Shimadzu SV-50A Spectrophotometer, IR spectra on a Nihon-Bunko DS-301 Spectrophotometer, ^1H NMR spectra on a Japan Electron Optics JNM C-60-H Spectrometer at 60 MHz with tetramethylsilane as an internal standard, mass spectra on a Japan Electron Optics Model JMS-O1SG Mass spectrometer.

4-Hydroxy-2-(*o*-chlorophenyl)-5-phenylthiazole (IVb)—Yellow prisms (from acetone), mp 209—211°, 69% yield. *Anal.* Calcd. for $C_{15}H_{10}ClNOS$: C, 62.60; H, 3.50; N, 4.87. Found: C, 62.66; H, 3.36; N, 4.77.

4-Hydroxy-2-(*p*-chlorophenyl)-5-phenylthiazole (IVc)—Yellow leaflets (from $CHCl_3$), mp 245—246°, 83% yield. *Anal.* Calcd. for $C_{15}H_{10}ClNOS$: C, 62.60; H, 3.50; N, 4.87. Found: C, 62.69; H, 3.26; N, 4.72.

4-Hydroxy-2-phenyl-5-(*p*-toluyl)-thiazole (IVd)—Yellow needles (from acetone), mp 227°, 70% yield. *Anal.* Calcd. for $C_{16}H_{13}NOS$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.98; H, 4.80; N, 4.93.

4-Hydroxy-2-(*p*-chlorophenyl)-5-(*p*-toluyl)-thiazole (IVe)—Yellow needles (from $CHCl_3$), mp 263—265°, 65% yield. *Anal.* Calcd. for $C_{16}H_{12}ClNOS$: C, 63.67; H, 4.01; N, 4.64. Found: C, 63.79; H, 4.12; N, 4.73.

Reaction of IIa—e with Acetic Anhydride to give Va—e besides IIIa—e

General Procedure—A solution of IIa—e (1 g) in Ac_2O (2 ml) was heated under the conditions described below respectively. The reaction mixture was treated in the same way as that of the reaction of IIa—e with Ac_2O to give IIIa—e. The $CHCl_3$ extract was chromatographed over silica gel (Silica gel 60, 70—230 mesh, E. MERCK) with petr. ether—ether. Each of the fractions was purified by fractional recrystallization.

Reaction of IIa—A solution of IIa in Ac_2O was heated at 100° for 2 hr. IIIa: 9% yield. Va-1: Colorless needles (from ether—petr. ether), mp 150°, 15% yield. *Anal.* Calcd. for $C_{19}H_{17}NO_4S$: C, 64.22; H, 4.82; N, 3.94. Found: C, 64.63; H, 4.39; N, 4.32. Va-2: Colorless plates (from ether—petr. ether), mp 123—124°, 28% yield. *Anal.* Calcd. for $C_{19}H_{17}NO_4S$: C, 64.22; H, 4.82; N, 3.94. Found: C, 64.49; H, 4.64; N, 3.70.

Reaction of IIb—A solution of IIb in Ac_2O and dioxane (15 ml) was heated at 100° for 2 hr. Ib: 8% yield. IIb: 7% yield. Vb-1: Colorless prisms (from ether—petr. ether), mp 100—102°, 17% yield. *Anal.* Calcd. for $C_{19}H_{16}ClNO_4S$: C, 58.53; H, 4.14; N, 3.59. Found: C, 58.21; H, 3.96; N, 3.76. Vb-2: Colorless needles (from ether—petr. ether), mp 96—97°, 30% yield. *Anal.* Calcd. for $C_{19}H_{16}ClNO_4S$: C, 58.53; H, 4.14; N, 3.59. Found: C, 58.29; H, 4.05; N, 3.86.

Reaction of IIc—Reaction Condition 1: A solution of IIc in Ac_2O was heated at 100° for 2 hr. Ic: 15% yield. IIc: 13% yield. Vc-1: Colorless prisms (from ether—petr. ether), mp 142—143°, 12% yield. *Anal.* Calcd. for $C_{19}H_{16}ClNO_4S$: C, 58.53; H, 4.14; N, 3.59. Found: C, 58.64; H, 4.00; N, 3.74. Vc-2: Colorless prisms (from ether—petr. ether), mp 155—156°, 27% yield. *Anal.* Calcd. for $C_{19}H_{16}ClNO_4S$: C, 58.53; H, 4.14; N, 3.59. Found: C, 58.71; H, 4.03; N, 3.82. Reaction condition 2: A solution of IIc in Ac_2O and dioxane (15 ml) was heated at 100° for 2 hr. Ic: 10% yield. IIc: 17% yield. Vc-1: 7% yield. Vc-2: 38% yield.

Reaction of IId—A solution of IId in Ac_2O and dioxane (15 ml) was heated at 100° for 2 hr. Id: 9% yield. IId: 8% yield. Vd-1: Colorless prisms (from ether—petr. ether), mp 144—145°, 4% yield. *Anal.* Calcd. for $C_{20}H_{19}NO_4S$: C, 65.03; H, 5.19; N, 3.79. Found: C, 65.27; H, 4.98; N, 3.61. Vd-2: Colorless needles (from ether—petr. ether), mp 136—137°, 33% yield. *Anal.* Calcd. for $C_{20}H_{19}NO_4S$: C, 65.03; H, 5.19; N, 3.79. Found: C, 65.31; H, 5.15; N, 3.85.

Reaction of IIe—A solution of IIe in Ac_2O and dioxane (15 ml) was heated at 100° for 2 hr. Ie: 5% yield. IIe: 28% yield. Ve-1: Colorless columns (from acetone—petr. ether), mp 163—165°, 7% yield. *Anal.* Calcd. for $C_{20}H_{18}ClNO_4S$: C, 59.47; H, 4.49; N, 3.47. Found: C, 59.53; H, 4.52; N, 3.54. Ve-2: Colorless prisms (from acetone—petr. ether), mp 152—153°, 32% yield. *Anal.* Calcd. for $C_{20}H_{18}ClNO_4S$: C, 59.47; H, 4.49; N, 3.47. Found: C, 59.33; H, 4.47; N, 3.39.

Transformation of Va-1 and Va-2 into IIIa in Acetic Anhydride

Reaction of Va-1—A solution of Va-1 (0.3 g) in 1 ml of Ac_2O was heated at 130° for 3 hr. The resulting mixture was treated in the same way as that of the reaction of IIa with Ac_2O to give IIIa. IIIa was obtained in 96% yield.

Reaction of Va-2—The reaction was carried out in the same way as that of Va-1. IIIa was obtained in 92% yield.

Pyrolysis of Va-1—Va-1 (0.2 g) was heated at 165° for 15 min. After cooling, the residue was recrystallized from ether—petr. ether to afford IIIa in an almost quantitative yield.

Pyrolysis of Va-2—This was carried out in the same way as that of Va-1. Only Va-1 was recovered quantitatively.

Acknowledgement The authors are grateful to Professor M. Hamana, Kyushu University, for his valuable discussions and encouragement throughout this work. Thanks are also due Japan Electron Optics Lab. Ltd. and Mr. M. Nishi, Fukuoka University, for mass spectral measurements and the members of the Analytical Center of the Faculty of Pharmaceutical Sciences, Kyushu University, for elemental analyses.