Synthesis of Arylthio-Substituted 3,8-Diphenyl-1,2-diazacycloocta-2,4,6,8-tetraenes and Their Thermolysis

Seiichi YOGI,* Kozo HOKAMA, and Otohiko TSUGE†,*
Department of Chemistry, Faculty of Science, Ryukyu University, Nakagami-gun, Okinawa 903-01
†Research Institute of Industrial Science, Kyushu University, Kasugakoen, Kasuga 816
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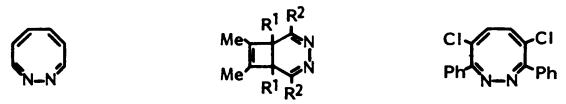
Nucleophilic substitution of 4,7-dichloro-3,8-diphenyl-1,2-diazocine with arenethiols gave stable 4-arylthio-7-chloro- and/or 4,7-bis(arylthio)-1,2-diazocines. Unsymmetrical 4,7-bis(arylthio)- and 4-acetoxy-7-phenylthio-1,2-diazocines were also prepared from 4-chloro-7-phenylthio-1,2-diazocine. Thermolysis of all the diazocines afforded only arylthio-substituted pyridines with extrusion of benzonitrile.

1,2-Diazacycloocta-2,4,6,8-tetraenes (1,2-diazocines) free of benzo groups were not known until Trost et al.[1] succeeded in an elegant synthesis of the parent 1,2-diazocine (**1**), which decomposed slowly in solution at room temperature and rapidly neat. However, experiments that might have yielded substituted monocyclic 1,2-diazocines, in which compound **2** had been pyrolyzed, failed to give stable eight-membered rings, for although these probably formed, under the conditions of their preparation they seemingly valence tautomerized and extruded nitrogen, giving substituted benzene instead.[2]



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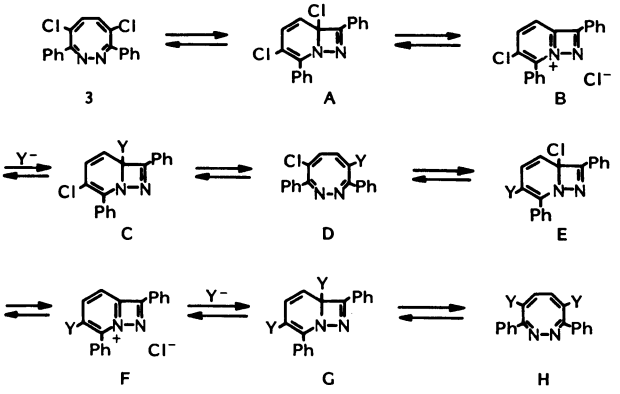
We have recently reported[3] a convenient method for the synthesis of 4,7-dichloro-3,8-diphenyl-1,2-diazocine (**3**), which is the first example of stable substituted monocyclic 1,2-diazocine, via a chlorination-dehydrochlorination sequence starting from readily available 3,8-diphenyl-1,2-diazacycloocta-2,8-diene,[4] and the conversion of **3** into stable mono(acyloxy)- and bis(acyloxy)-1,2-diazocines by nucleophilic substitutions of chlorine atoms on **3** with carboxylate anions. In addition, it has been found that in contrast to the parent 1,2-diazocine (**1**), which thermally decomposed to benzene and pyridine with comparable rates,[1] these stable 1,2-diazocines had been pyrolyzed to give only pyridines with the extrusion of benzonitrile: This provided a new route for the synthesis of chloro- and acyloxy-substituted pyridines which are difficult to prepare by other methods.

Nucleophilic substitutions of chlorine atoms on the 1,2-diazocine (**3**) with a carboxylate anion (Y=OCOR) can be understood by the processes as illustrated in Scheme 1. The 1,2-diazocine (**3**) is thermally isomerized into its valence isomer (**A**), which gives a mono(acyloxy)-1,2-diazocine (**D**) through the process **B**→**C**, and then the 1,2-diazocine (**D**) is similarly converted into a bis(acyloxy)-1,2-diazocine (**H**) via the processes **E**→**F**→**G**.[3]

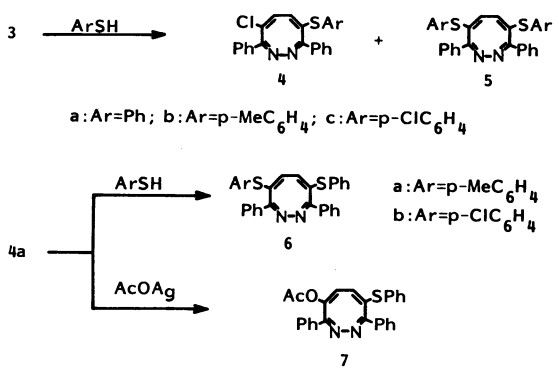
Thus, it is indicated that a route to new 4,7-disubstituted 1,2-diazocines is opened by the reaction of 4,7-dichloro-1,2-diazocine (**3**) with various nucleophiles. In this paper we describe the synthesis of arylthio-substituted 1,2-diazocines, and their thermolysis leading to pyridines.

Results and Discussion

Synthesis of Arylthio-Substituted 1,2-Diazocines. Although the reaction of 4,7-dichloro-1,2-diazocine (**3**) with sodium benzenethiolate in benzene under reflux gave the expected 4-chloro-7-phenylthio- (**4a**) and 4,7-



Scheme 1.

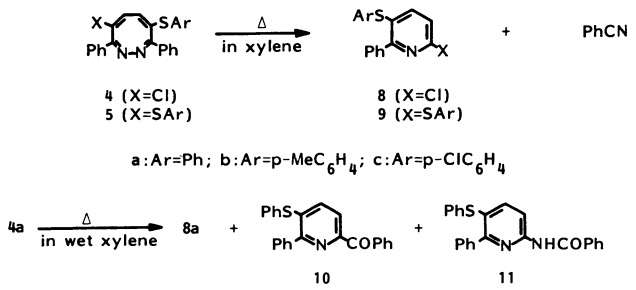


Scheme 2.

bis(phenylthio)-1,2-diazocine (**5a**), the reaction using benzenethiol in place of the thiolate brought about more satisfactory results. When heated with four equivalents of benzenethiol under similar conditions, **3** was converted into a mixture of **4a** and **5a** in good yield, whose relative yields depended upon the reaction time. Similarly, the 1,2-diazocine (**3**) reacted with *p*-methyl- and *p*-chlorobenzenethiol to give the corresponding mono(arylthio)- (**4b** and **4c**) and bis-(arylthio)-1,2-diazocines (**5b** and **5c**), respectively.[5] The results are given in Table 1.

In the reaction of mono(phenylthio)-1,2-diazocine (**4a**) with *p*-substituted benzenethiols under similar conditions, the corresponding unsymmetrical bis-(arylthio)-1,2-diazocines (**6a** and **6b**) were obtained in good yields, respectively. A longer reaction time was required for the preparation of **6a** than for **6b** (Table 1). Also, the 1,2-diazocine (**4a**) reacted with silver acetate in refluxing benzene to give 4-acetoxy-7-phenylthio-1,2-diazocine (**7**) (Scheme 2). Structural elucidation of all the 1,2-diazocines (**4**—**7**) was accomplished on the basis of spectral data.

Thermolysis of Arylthio-Substituted 1,2-Diazocines. It is evident that the mono(arylthio)- (**4**) and bis(arylthio)-1,2-diazocines (**5**) are thermally isomerized into their valence isomers, diazabicyclooctatrienes like **E** and **G** (Y=ArS), respectively (Scheme 1). Thus, in analogy with acyloxy-substituted 1,2-diazocines,[3] thermolysis of the 1,2-diazocines (**4** and **5**) can be expected to afford mono(arylthio)- and bis(arylthio)-substituted pyridines with the extrusion of benzonitrile, respectively.



Scheme 3.

In fact, the 1,2-diazocines (**4** and **5**) decomposed in dry xylene under reflux to give the corresponding 3-arylthio-6-chloro-2-phenylpyridine (**8**) and 3,6-bis-(arylthio)-2-phenylpyridines (**9**) in good yields respectively, together with benzonitrile (Table 2). On the other hand, when heated in wet xylene under reflux for 6 h, the 1,2-diazocine (**4a**) afforded the pyridine (**8a**), 6-benzoyl-2-phenyl-3-phenylthiopyridine (**10**), and 6-benzoylamino-2-phenyl-3-phenylthiopyridine (**11**) in 12, 63, and 7% yields, respectively (Scheme 3): This is closely similar to the formation of 3,6-dichloro-2-phenyl-, 6-benzoyl-3-chloro-2-phenyl-, and 6-benzoyl-amino-3-chloro-2-phenylpyridine in the thermolysis of 4,7-dichloro-1,2-diazocine (**3**) in wet toluene.[3]

The structures of pyridines (**8**—**11**) were confirmed on the basis of spectral data as well as on the chemical conversions.

The mono(phenylthio)pyridine (**8a**) was allowed to react with sodium methoxide in methanol under reflux to give 6-methoxy-2-phenyl-3-phenylthiopyridine (**12**), which on heating with hydrobromic acid was converted into a mixture of 6-phenyl-2-pyridone (**13**)[6] and diphenyl disulfide. The pyridone (**13**) was

Table 2. Thermolysis of Arylthio-Substituted 1,2-Diazocines[a]

1,2-Diazocine	Reaction time/h	Products/%	
		Pyridine	PhCN
4a	5	**8a** 75	93
4b	6	**8b** 73	63
4c	6	**8c** 86	72
5a	6	**9a** 85	93
5b	6	**9b** 92	78
5c	6	**9c** 79	84

a) The thermolysis was carried out in dry xylene under reflux.

Table 1. Reactions of Chloro-Substituted 1,2-Diazocines with Nucleophiles[a]

Starting Diazocine (SD)	Nucleophile (Nu)	SD/Nu mol/mol	Reaction time/h	Products yield/%	Unreacted SD/%
3	PhSNa	1/3	5	**4a** 38 **5a** 17	15
3	PhSH	1/4	6	**4a** 65 **5a** 32	3
3	PhSH	1/4	18	**4a** 2 **5a** 70	2
3	*p*-MeC_6H_4SH	1/4	4	**4b** 59 **5b** 12	28
3	*p*-MeC_6H_4SH	1/4	18	**5b** 98	0
3	*p*-ClC_6H_4SH	1/3	7	**4c** 43 **5c** 34	—[b]
4a	*p*-MeC_6H_4SH	1/1.5	7	**6a** 35	41
4a	*p*-MeC_6H_4SH	1/3	24	**6a** 78	—[b]
4a	*p*-ClC_6H_4SH	1/1.5	7	**6b** 75	8
4a	MeCOOAg	1/4.8	20	**7** 61	20

a) The reactions were carried out in benzene under reflux. b) The unreacted diazocine was not isolated.

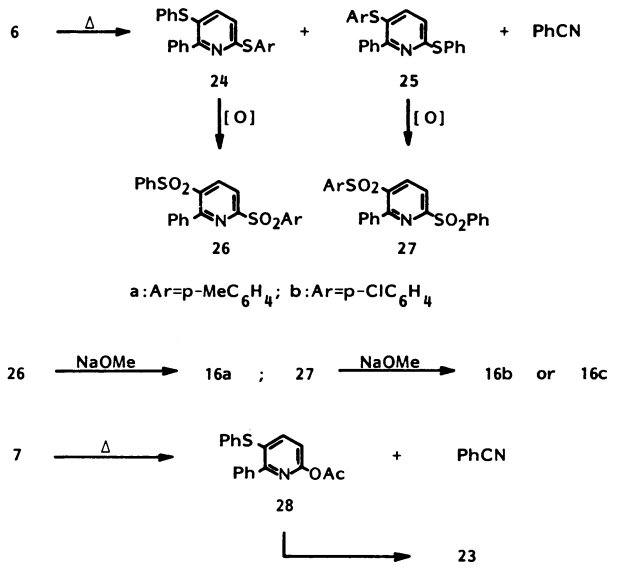
identical with an authentic sample prepared from hydrolysis of 2-acetoxy-6-phenylpyridine.[7]

Oxidations of the mono(arylthio)- (**8**) and bis(arylthio)pyridines (**9**) with potassium permanganate in acetic acid or 35% hydrogen peroxide gave the corresponding mono(arylsulfonyl) (**14**) and bis(arylsulfonyl)pyridines (**15**) in good yields, respectively. On treatment with sodium methoxide in methanol under reflux, both the pyridines (**14** and **15**) were converted into the same 3-arylsulfonyl-6-methoxy-2-phenylpyridines (**16**). When heated with hydrobromic acid, 6-methoxy-2-phenyl-3-phenylsulfonylpyridine (**16a**) was converted into 6-phenyl-5-phenylsulfonyl-2-pyridone (**17**) (Scheme 4).

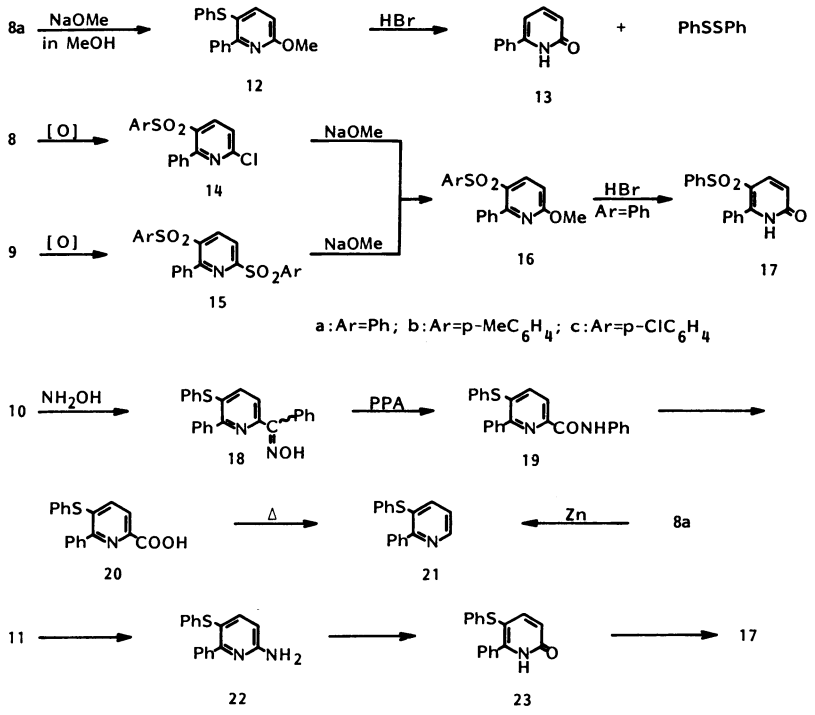
On the other hand, the reaction of the benzoylpyridine (**10**) with hydroxylamine afforded a mixture of stereoisomeric oximes (**18**), which on the Beckmann rearrangement using polyphosphoric acid gave 2-phenyl-6-phenylcarbamoyl-3-phenylthiopyridine (**19**) in good yield. Hydrolysis of the pyridine (**19**) gave 6-phenyl-5-phenylthio-2-pyridinecarboxylic acid (**20**), which on heating at 230—250 °C was converted into 2-phenyl-3-phenylthiopyridine (**21**). The pyridine (**21**) was also obtained by the reduction of the pyridine (**8a**) with zinc dust in acetic acid.

Hydrolysis of the (benzoylamino)pyridine (**11**) with an ethanolic alkali solution gave 6-amino-2-phenyl-3-phenylthiopyridine (**22**), which was then converted, by diazotization, into 6-phenyl-5-phenylthio-2-pyridone (**23**). Oxidation of the pyridone (**23**) gave the phenylsulfonylpyridone (**17**).

Next, thermolysis of unsymmetrical bis(arylthio)-1,2-diazocines (**6**) was investigated. In dry xylene under reflux for 5 h, the 4-(*p*-methylphenylthio)-7-phenylthio-1,2-diazocine (**6a**) gave benzonitrile and oil, which consisted of a 1:1 mixture of 6-(*p*-methylphenylthio)-2-phenyl-3-phenylthio- (**24a**) and 3-(*p*-methylphenylthio)-2-phenyl-6-phenylthiopyridine (**25a**), in 78 and 68% yields, respectively. Although it was very difficult to isolate pure **24a** and **25a** from the mixture, the formation of **24a** and **25a** was confirmed by the conversion, via the corresponding bis(arylsulfonyl)pyridines (**26a** and **27a**),



Scheme 5.



Scheme 4.

into the methoxypyridines (**17a** and **17b**), respectively.

Similarly, thermolysis of the 4-(*p*-chlorophenylthio)-7-phenylthio-1,2-diazocine (**6b**) afforded benzonitrile and a mixture of 6-(*p*-chlorophenylthio)-2-phenyl-3-phenylthio- (**24b**) and 3-(*p*-chlorophenylthio)-2-phenyl-6-phenylthiopyridine (**25b**) in 76 and 84% yields, respectively. The pyridines (**24b** and **25b**) were again converted into the methoxypyridines (**17a** and **17c**) via the corresponding bis(arylsulfonyl)pyridines (**26b** and **27b**), respectively (Scheme 5).

Thermolysis of the 4-acetoxy-7-phenylthio-1,2-diazocine (**7**) was performed under similar conditions: Benzonitrile and 6-acetoxy-2-phenyl-3-phenylthiopyridine (**28**) were obtained in 69 and 87% yields, respectively. The acetoxypyridine (**28**) was readily converted into the pyridone (**23**) on an ethanolic alkali hydrolysis.

Experimental

IR spectra were obtained on a JASCO A-302 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-24 or a JEOL FX-100 instrument, and ^{13}C NMR spectra were measured on a JEOL FX-100 spectrometer at 25.05 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane. Mass spectra were taken with a Hitachi RMU-6L spectrometer at 70 eV ionization energy. Elemental analyses were performed on a Yanaco MT 2 CHN corder instrument.

Reaction of Dichloro-1,2-diazocine (3) with Sodium Benzenethiolate. A solution of benzenethiol (1.10 g, 10 mmol) in methanol (10 ml) was added to a solution of sodium methoxide in methanol, which was prepared from metallic sodium (0.3 g) and methanol (10 ml), and then the resultant mixture was concentrated in vacuo to leave sodium benzenethiolate as white powder. A solution of 1.08 g (3.3 mmol) of the dichloro-1,2-diazocine (**3**) in benzene (50 ml) was refluxed with the thiolate for 5 h. The reaction mixture was washed with water, and the benzene layer was concentrated in vacuo, and the residue was chromatographed on silica gel using benzene–hexane (3:7) as an eluent to give 0.17 g (15%) of unreacted **3**, 0.42 g (38%) of the mono(phenylthio)-1,2-diazocine (**4a**) and 0.23 g (17%) of the bis(phenylthio)-1,2-diazocine (**5a**).

4a: Mp 143—144 °C (decomp); colorless needles; ^{1}H NMR ($CDCl_3$) δ=6.17, 6.49 (each 1H, d, =CH, J=4.8 Hz), 7.10—7.50 (13H, m), 7.51—7.80 (2H, m); MS m/z 402, 400 (M^+). Found: C, 71.98; H, 4.26; N, 7.11%. Calcd for $C_{24}H_{17}N_2SCl$: C, 71.90; H, 4.27; N, 6.99%.

5a: Mp 156—157 °C; colorless needles; ^{1}H NMR ($CDCl_3$) δ=6.27 (2H, s, =CH), 7.00—7.50 (16H, m), 7.51—7.70 (4H, m); ^{13}C NMR ($CDCl_3$) δ=153.47 (s), 137.56 (s), 134.80 (s), 132.80 (s), 131.80, 129.99, 129.16, 128.34, 128.22 (each d); MS m/z 474 (M^+). Found: C, 75.80; H, 4.62; N, 6.08%. Calcd for $C_{30}H_{22}N_2S_2$: C, 75.92; H, 4.67; N, 5.90%.

Reaction of 3 with Arenethiols. i) With Benzenethiol. After a solution of **3** (0.65 g, 2 mmol) and benzenethiol (0.88 g, 8 mmol) in benzene (50 ml) was refluxed for 6 h, the reaction mixture was washed with a 10% aqueous sodium hydroxide solution, and then water. The benzene layer was concentrated in vacuo, and the residue was chromatographed (silica gel, benzene) to give 20 mg (3%) of unreacted **3**, 0.52 g (65%) of **4a** and 0.30 g (32%) of **5a**. The result of the reaction for 18 h is shown in Table 1.

ii) With *p*-Methylbenzenethiol. A solution of **3** (0.65 g, 2 mmol) in benzene (30 ml) refluxed with *p*-methylbenzenethiol (1.0 g, 8 mmol) for 4 h. Similar work-up of the reaction mixture gave 0.18 g (28%) of unreacted **3**, 0.49 g (59%) of the mono(*p*-methylphenylthio)-1,2-diazocine (**4b**), and 0.12 g (12%) of the bis(*p*-methylphenylthio)-1,2-diazocine (**5b**). The result of the reaction for 18 h is given in Table 1.

4b: Mp 131—132 °C; colorless prisms; ^{1}H NMR ($CDCl_3$) δ=2.28 (3H, s), 6.10, 6.50 (each 1H, d, =CH, J=4.2 Hz), 6.80—7.80 (14H, m); MS m/z, 416, 414 (M^+). Found: C, 72.48; H, 4.46; N, 6.70%. Calcd for $C_{25}H_{19}N_2SCl$: C, 72.36; H, 4.62; N, 6.75%.

5b: Mp 172—173 °C; colorless needles; ^{1}H NMR ($CDCl_3$) δ=2.26 (6H, s), 6.20 (2H, s, =CH), 6.80—7.80 (18H, m); MS m/z 502 (M^+). Found: C, 76.58; H, 5.26; N, 5.34%. Calcd for $C_{32}H_{26}N_2S_2$: C, 76.45; H, 5.21; N, 5.57%.

iii) With *p*-Chlorobenzenethiol. A solution of **3** (1.2 g, 3.68 mmol) in benzene (30 ml) was refluxed with *p*-chlorobenzenethiol (1.59 g, 11 mmol) for 7 h. Similar work-up gave 0.68 g (43%) of the mono(*p*-chlorophenylthio)-1,2-diazocine (**4c**) and 0.67 g (34%) of the bis(*p*-chlorophenylthio)-1,2-diazocine (**5c**).

4c: Mp 99—101 °C; colorless needles; ^{1}H NMR ($CDCl_3$) δ=6.18, 6.42 (each 1H, d, =CH, J=4.2 Hz), 7.03 (4H, s), 7.16—7.86 (10H, m); MS m/z 438, 436, 434 (M^+). Found: C, 66.39; H, 3.78; N, 6.56%. Calcd for $C_{24}H_{16}N_2SCl_2$: C, 66.21; H, 3.70; N, 6.43%.

5c: Mp 196—197 °C (decomp); yellow needles; ^{1}H NMR ($CDCl_3$) δ=6.32 (2H, s, =CH), 7.15 (8H, s), 7.20—7.70 (10H, m); MS m/z 546, 544, 542 (M^+). Found: C, 66.57; H, 3.46; N, 4.92%. Calcd for $C_{30}H_{20}N_2S_2Cl_2$: C, 66.29; H, 3.71; N, 5.15%.

4-(*p*-Methylphenylthio)-7-phenylthio-1,2-diazocine (6a). A solution of 1.0 g (2.5 mmol) of the mono(phenylthio)-1,2-diazocine (**4a**) in benzene (50 ml) was refluxed with *p*-methylbenzenethiol (1.0 g, 8.1 mmol) for 24 h. Similar work-up gave 0.95 g (78%) of the diazocine (**6a**): Mp 132—133 °C; colorless needles; ^{1}H NMR ($CDCl_3$) δ=2.22 (3H, s), 6.15, 6.24 (each 1H, d, =CH, J=4.2 Hz), 6.75—7.90 (19H, m); MS m/z 488 (M^+). Found: C, 76.02; H, 4.90; N, 5.82%. Calcd for $C_{31}H_{24}N_2S_2$: C, 76.20; H, 4.95; N, 5.73%.

The result of the reaction for 7 h is given in Table 1.

4-(*p*-Chlorophenylthio)-7-phenylthio-1,2-diazocine (6b). A solution of 0.64 g (1.6 mmol) of the diazocine (**4a**) in benzene (30 ml) was refluxed with *p*-chlorobenzenethiol (0.35 g, 2.4 mmol) for 7 h. Similar work-up afforded 50 mg (8%) of unreacted **4a** and 0.61 g (75%) of the diazocine (**6b**): Mp 129—130 °C; yellow needles; ^{1}H NMR ($CDCl_3$) δ=6.30, 6.37 (each 1H, d, =CH, J=4.2 Hz), 7.03—7.73 (19H, m); MS m/z 510, 508 (M^+). Found: C, 70.68; H, 3.94; N, 5.61%. Calcd for $C_{30}H_{21}N_2S_2Cl$: C, 70.78; H, 4.16; N, 5.50%.

4-Acetoxy-7-phenylthio-1,2-diazocine (7). A solution of 1.0 g (2.5 mmol) of the diazocine (**4a**) in benzene (50 ml) was refluxed with silver acetate (2.0 g, 12 mmol) for 20 h. The reaction mixture was filtered, and the precipitate was washed with benzene (50ml). The combined benzene solution was concentrated in vacuo, and the residue was chromatographed (silica gel, benzene) to give 0.2 g (20%) of

unreacted **4a** and 0.65 g (61%) of the diazocine (**7**): Mp 161—163 °C (decomp); colorless needles; ^{1}H NMR ($CDCl_3$) δ=1.95 (3H, s), 6.25 (2H, s, =CH), 7.20—7.90 (15H, m); MS *m/z* 425 (M^+). Found: C, 73.31; H, 4.51; N, 6.74%. Calcd for $C_{26}H_{20}N_2O_2S$: C, 73.56; H, 4.75; N, 6.60%.

Thermolysis of 4-Chloro-7-phenylthio-1,2-diazocine (4a). i) In Dry Xylene. A solution of **4a** (1.60 g, 4 mmol) in dry xylene (20 ml) was refluxed for 5 h. The reaction mixture was concentrated in vacuo, and the residue was chromatographed (silica gel, benzene) to give 0.38 g (93%) of benzonitrile and 0.89 g (75%) of 6-chloro-2-phenyl-3-phenylthiopyridine (**8a**).

8a: Oil; ^{1}H NMR ($CDCl_3$) δ=7.06, 7.53 (each 1H, d, PyH, *J*=8.0 Hz), 7.20—7.90 (10H, m); MS *m/z* 299, 297 (M^+). Found: C, 68.85; H, 4.05; N, 4.91%. Calcd for $C_{17}H_{12}NSCl$: C, 68.56; H, 4.06; N, 4.70%.

Thermolysis of 4-chloro-7-(*p*-methylphenylthio)- (**4b**) and 4-chloro-7-(*p*-chlorophenylthio)-1,2-diazocine (**4c**) under similar conditions afforded 6-chloro-3-(*p*-methylphenylthio)-2-phenyl- (**8b**) and 6-chloro-3-(*p*-chlorophenylthio)-2-phenylpyridine (**8c**) together with benzonitrile, respectively. The results are shown in Table 2.

8b: Oil; ^{1}H NMR ($CDCl_3$) δ=2.31 (3H, s), 6.98 (1H, d, PyH, *J*=8.4 Hz), 7.02—7.82 (10H, m, ArH and PyH); MS *m/z* 311 (M^+). Found: C, 69.54; H, 4.34; N, 4.65%. Calcd for $C_{18}H_{14}NSCl$: C, 69.33; H, 4.53; N, 4.49%.

8c: Oil; ^{1}H NMR ($CDCl_3$) δ=7.08 (1H, d, PyH, *J*=8.4 Hz), 7.10—7.80 (10H, m, ArH and PyH); MS *m/z* 335, 333, 331 (M^+). Found: C, 61.20; H, 3.61; N, 4.08%. Calcd for $C_{17}H_{11}NSCl_2$: C, 61.45; H, 3.34; N, 4.22%.

ii) In Wet Xylene. A solution of **4a** (1.60 g, 4 mmol) in xylene (20 ml) containing 3 drops of water was refluxed for 6 h. Similar work-up and chromatography (silica gel, benzene) of the pyrolysate gave 0.14 g (12%) of the pyridine (**8a**), 0.92 g (63%) of 6-benzoyl-2-phenyl-3-phenylthiopyridine (**10**) and 0.11 g (7%) of 6-benzoylamino-2-phenyl-3-phenylthiopyridine (**11**).

10: Mp 120—121 °C; colorless prisms; IR (KBr) 1646 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.21 (5H, s), 7.65, 8.23 (each 1H, d, PyH, *J*=8.2 Hz), 7.30—7.65 (8H, m), 7.80—8.02 (2H, m); MS *m/z* 367 (M^+). Found: C, 78.32; H, 4.59; N, 3.50%. Calcd for $C_{24}H_{17}NOS$: C, 78.44; H, 4.66; N, 3.81%.

11: Mp 120—121 °C; yellow prisms; IR (KBr) 3300, 3200, 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.04—8.04 (16H, m, ArH and PyH), 8.29 (1H, d, PyH, *J*=8.4 Hz), 8.74 (1H, broad, NH); MS *m/z* 382 (M^+). Found: C, 75.14; H, 4.91; N, 7.10%. Calcd for $C_{24}H_{18}N_2OS$: C, 75.36; H, 4.74; N, 7.33%.

Thermolysis of 4,7-Bis(phenylthio)-1,2-diazocine (5a). A solution of 0.95 g (2 mmol) of the diazocine (**5a**) in dry xylene (20 ml) was refluxed for 6 h. Similar work-up and chromatography (silica gel, benzene) of the pyrolysate gave 0.19 g (93%) of benzonitrile and 0.63 g (85%) of 3,6-bis(phenylthio)-2-phenylpyridine (**9a**).

9a: Mp 77—78 °C; colorless prisms; ^{1}H NMR ($CDCl_3$) δ=6.61 (1H, d, PyH, *J*=7.2 Hz), 7.10—7.80 (16H, m, ArH and PyH); MS *m/z* 371 (M^+). Found: C, 74.40; H, 4.31; N, 3.79%. Calcd for $C_{23}H_{17}NS_2$: C, 74.35; H, 4.61; N, 3.77%.

Similar thermolysis of 4,7-bis(*p*-methylphenylthio)- (**5b**) and 4,7-bis(*p*-chlorophenylthio)-1,2-diazocine (**5c**) afforded 3,6-bis(*p*-methylphenylthio)-2-phenyl- (**9b**) and 3,6-bis(*p*-chlorophenylthio)-2-phenylpyridine (**9c**), together with benzonitrile, respectively. The results are given in Table 2.

9b: Mp 102—103 °C; colorless prisms; ^{1}H NMR ($CDCl_3$) δ=2.29, 2.45 (each 3H, s), 6.57 (1H, d, PyH, *J*=8.4 Hz), 7.02—8.03 (14H, m, ArH and PyH); MS *m/z* 399 (M^+). Found: C, 74.97; H, 5.51; N, 3.53%. Calcd for $C_{25}H_{21}NS_2$: C, 75.14; H, 5.30; N, 3.51%.

9c: Oil; ^{1}H NMR ($CDCl_3$) δ=6.67 (1H, d, PyH, *J*=8.4 Hz), 7.10—7.70 (14H, m, ArH and PyH); MS *m/z* 443, 441, 439 (M^+). Found: C, 62.81; H, 3.17; N, 3.20%. Calcd for $C_{23}H_{15}NS_2Cl_2$: C, 62.72; H, 3.43; N, 3.18%.

6-Methoxy-2-phenyl-3-phenylthiopyridine (12). In a solution of sodium methoxide in methanol, which was prepared from metallic sodium (1.0 g) in methanol (30 ml), 0.5 g (1.7 mmol) of the pyridine (**8a**) was heated under reflux for 5 h. The reaction mixture was poured into water (100 ml), and the mixture was extracted with benzene (50 ml×2). The extract was concentrated in vacuo, and the residue was chromatographed (silica gel, benzene) to give 0.41 g (82%) of the methoxypyridine (**12**): Mp 68—69 °C; colorless prisms; ^{1}H NMR ($CDCl_3$) δ=3.85 (3H, s), 6.54, 7.48 (each 1H, d, PyH, *J*=8.4 Hz), 7.13—7.38 (3H, m), 7.02 (5H, s), 7.53—7.73 (2H, m); MS *m/z* 293 (M^+). Found: C, 73.58; H, 5.02; N, 4.60%. Calcd for $C_{18}H_{15}NOS$: C, 73.69; H, 5.15; N, 4.77%.

Conversion of the Methoxypyridine (12) into 6-Phenyl-2-pyridone (13). A suspension of 0.15 g (0.5 mmol) of the pyridine (**12**) in 48% hydrobromic acid (1 ml) was heated under reflux for 4 h. To the reaction mixture was added water (10 ml), and the mixture was extracted with benzene. The benzene extract was concentrated in vacuo, and the residue was chromatographed (silica gel, benzene) to give 30 mg (27%) of diphenyl disulfide which was identical with an authentic sample. An aqueous acidic layer was alkalized with an aqueous sodium carbonate solution to precipitate 40 mg (46%) of the pyridine (**13**), mp 196—197 °C (lit,[6] mp 197 °C), which was identical with an authentic sample prepared from hydrolysis of 2-acetoxy-6-phenylpyridine.[7]

6-Chloro-2-phenyl-3-phenylsulfonylpyridine (14a). To a stirred solution of 0.3 g (1 mmol) of the phenylthiopyridine (**8a**) in acetic acid (30 ml), added slowly a 6.6% aqueous potassium permanganate solution at room temperature; when about 5 ml of the permanganate solution was added, reddish violet color of the reaction mixture did not disappear. A 10% aqueous sodium hydrogensulfite solution (10 ml) was added to the colored solution, and then the resultant clear solution was poured into water (50 ml) to give a precipitate. Filtration and recrystallization of the precipitate from petroleum ether to give 0.27 g (82%) of the phenylsulfonylpyridine (**14a**): Mp 131—133 °C; colorless needles; IR (KBr) 1320 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.05—7.45 (10H, m), 7.47, 8.65 (each 1H, d, PyH, *J*=8.4 Hz); ^{13}C NMR ($CDCl_3$) δ=159.75, 154.40, 139.67, 139.32, 136.44, 133.81, 129.57, 129.22, 128.52, 127.87, 127.64, 123.17; MS *m/z* 331, 329 (M^+). Found: C, 61.75; H, 3.97; N, 4.43%. Cacld for $C_{17}H_{12}NO_2SCl$: C, 61.91; H, 3.67; N, 4.25%.

Similar oxidations of *p*-methylphenylthio- (**8b**) and *p*-chlorophenylthiopyridine (**8c**) gave the corresponding arylsulfonylpyridines **14b** and **14c** in 61 and 76% yields, respectively.

14b: Mp 143—145 °C; colorless needles; IR (KBr) 1320 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.33 (3H, s), 6.95—7.45 (9H, m), 7.51, 8.62 (each 1H, d, PyH, *J*=8.4 Hz); MS *m/z* 345, 343 (M^+). Found: C, 62.66; H, 3.91; N, 3.78%. Calcd for

$C_{18}H_{14}NO_2SCl$: C, 62.88; H, 4.10; N, 4.07%.

14c: Mp 149—150 °C; colorless needles; IR (KBr) 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.13—7.43 (9H, m), 7.55, 8.65 (each 1H, d, PyH, J=8.4 Hz); MS m/z 367, 365, 363 (M^+). Found: C, 56.27; H, 2.99; N, 3.61%. Calcd for $C_{17}H_{11}NO_2SCl_2$: C, 56.06; H, 3.04; N, 3.85%.

3,6-Bis(phenylsulfonyl)-2-phenylpyridine (15a). i) A solution of 0.50 g (1.4 mmol) of the bis(phenylthio)pyridine (**9a**) in acetic acid (30 ml) was refluxed with 35% hydrogen peroxide (5 ml) for 3 h. After it had been cooled to room temperature, water (100 ml) was added to it. The mixture was extracted with benzene (50 ml×2), and the extract was concentrated in vacuo to leave a residue which was recrystallized from petroleum ether to give 0.48 g (81%) of the pyridine (**15a**): Mp 187—189 °C; yellow needles; IR (KBr) 1320 cm^{-1}: ^1H NMR ($CDCl_3$) δ=7.20—7.72 (13H, m), 7.96—8.01 (2H, m), 8.32, 8.88 (each 1H, d, PyH, J=8.4 Hz); ^{13}C NMR ($CDCl_3$) δ=160.98, 159.75, 140.20, 139.55, 138.56, 136.33, 134.22, 133.51, 129.87, 129.39, 129.10, 128.63, 128.05, 127.52, 120.30; MS m/z 371 ($M^+ - SO_2$). Found: C, 63.51; H, 4.17; N, 3.28%. Cacld for $C_{23}H_{17}NO_4S_2$: C, 63.43; H, 3.93; N, 3.22%.

ii) A 6.6% aqueous potassium permanganate solution was slowly added, at room temperature, to a stirred solution of 0.37 g (1 mmol) of the pyridine (**9a**) in acetic acid (30 ml); when about 9 ml of the permanganate solution was added, reddish violet color of the reaction mixture did not disappear. After a 10% aqueous sodium hydrogensulfite solution (20 ml) was added to the reaction mixture, the resultant clear solution was poured into water (50 ml) to give a precipitate. Filtration and recrystallization of the precipitate from petroleum ether to give 0.28 g (64%) of the pyridine (**15a**).

Similar oxidations of the bis(*p*-methylphenylthio)- (**9b**) and bis(*p*-chlorophenylthio)pyridine (**9c**) with potassium permanganate in acetic acid gave the corresponding bis(arylsulfonyl)pyridines **15b** and **15c** in 69 and 76% yields, respectively.

15b: Mp 231—232 °C; colorless needles; IR (KBr) 1330 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.31, 2.39 (each 3H, s), 6.91—7.46 (11H, m), 7.71—8.01 (2H, m), 8.26, 8.86 (each 1H, d, PyH, J=8.4 Hz); MS m/z 399 ($M^+ - SO_2$). Found: C, 64.66; H, 4.70; N, 3.28%. Calcd for $C_{25}H_{21}NO_4S_2$: C, 64.77; H, 4.57; N, 3.02%.

15c: Mp 227—228 °C; colorless needles; IR (KBr) 1330 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.02—7.62 (11H, m), 7.82—8.02 (2H, m), 8.30, 8.88 (each 1H, d, PyH, J=8.4 Hz); MS m/z 443, 441, 439 ($M^+ - SO_2$). Found: C, 54.72; H, 2.79; N, 2.70%. Calcd for $C_{23}H_{15}NO_4S_2Cl_2$: C, 54.77; H, 3.00; N, 2.78%.

6-Methoxy-2-phenyl-3-phenylsulfonylpyridine (16a). i) In a solution of sodium methoxide in methanol, which was prepared from metallic sodium (1.0 g) in methanol (30 ml), 0.66 g (2 mmol) of the pyridine (**14a**) was refluxed for 5 h. The mixture was poured into water (100 ml), and extracted with benzene (50 ml×2). The benzene extract was concentrated in vacuo, and the residue was chromatographed (silica gel, benzene) to give 0.52 g (80%) of the pyridine (**16a**): Mp 84—85 °C; yellow prisms; IR (KBr) 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.90 (3H, s), 6.84, 8.52 (each 1H, d, PyH, J=8.4 Hz), 7.10—7.50 (10H, m); MS m/z 325 (M^+). Found: C, 66.51; H, 4.89; N, 4.33%. Calcd for $C_{18}H_{15}NO_3S$: C, 66.44; H, 4.65; N, 4.31%.

ii) In a solution of sodium methoxide in methanol, which was prepared from metallic sodium (0.5 g) in methanol (30 ml), 0.40 g (0.9 mmol) of the pyridine (**15a**) was refluxed for 5 h. Similar work-up and chromatography (silica gel, benzene) of the residue gave 0.22 g (75%) of the pyridine (**16a**).

The bis(*p*-methylphenylsulfonyl)- (**15b**) and bis(*p*-chlorophenylsulfonyl)pyridine (**15c**) reacted with sodium methoxide in methanol under similar conditions to give the corresponding methoxypyridines **16b** and **16c** in 67 and 70% yields, respectively.

16b: Mp 107—108 °C; colorless prisms; IR (KBr) 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.32 (3H, s), 3.92 (3H, s, OCH_3), 6.83, 8.50 (each 1H, d, PyH, J=8.4 Hz), 6.95—7.35 (9H, m); MS m/z 339 (M^+). Found: C, 67.41; H, 4.99; N, 4.34. Calcd for $C_{19}H_{17}NO_3S$: C, 67.23; H, 5.05; N, 4.13%.

16c: Mp 143—144 °C; colorless prisms; IR (KBr) 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.90 (3H, s), 6.79, 8.46 (each 1H, d, PyH, J=8.4 Hz), 7.02—7.30 (9H, m); MS m/z 361, 359 (M^+). Found: C, 59.87; H, 3.79; N, 3.74%. Calcd for $C_{18}H_{14}NO_3SCl$: C, 60.08; H, 3.92; N, 3.89%.

6-Phenyl-5-phenylsulfonyl-2-pyridone (17). A suspension of 0.16 g (0.5 mmol) of the methoxypyridine (**16a**) in 48% hydrobromic acid (4 ml) was refluxed for 4 h; during which time it turned into a clear solution. When it had been cooled to room temperature, crystals separated out. The crystals were filtered and washed well with a 10% aqueous sodium carbonate solution, and recrystallized from ethyl acetate to give 60 mg (40%) of the pyridone (**17**): Mp 267—268 °C; colorless needles; IR (KBr) 2700—3100, 1660, 1650, 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.41, 8.15 (each 1H, d, PyH, J=11.0 Hz), 7.10—7.50 (10H, m); MS m/z 311 (M^+). Found: C, 65.31; H, 4.00; N, 4.63%. Calcd for $C_{17}H_{13}NO_3S$: C, 65.58; H, 4.21; N, 4.50%.

Conversion of 6-Benzoyl-2-phenyl-3-phenylthiopyridine (10) into 2-Phenyl-6-phenylcarbamoyl-3-phenylthiopyridine (19). A solution of 0.49 g of the benzoylpyridine (**10**) in ethanol (30 ml) was refluxed with an aqueous hydroxylamine solution, which was prepared by the treatment of hydroxylamine hydrochloride (1.5 g) with a 7% aqueous sodium hydroxide solution (10 ml), for 2 h. The reaction mixture was poured into water (100 ml), and the resultant mixture was acidified with hydrochloric acid, and then extracted with chloroform (50 ml×2). The chloroform extract was concentrated in vacuo, and the residue was chromatographed (silica gel, chloroform) to give 0.27 g (54%) of a mixture of isomeric oximes (**18**). Without further purification, a mixture of oximes (**18**) was used for the Beckmann rearrangement: 0.3 g (0.8 mmol) of the oximes (**18**) was heated with polyphosphoric acid (3 ml) at 90—100 °C for 2 h. The mixture was poured into water (50 ml), and extracted with chloroform (30 ml×2). The extract was concentrated in vacuo, and the residue was chromatographed (silica gel, benzene) to give 0.24 g (88%) of the phenylcarbamoylpyridine (**19**).

19: Mp 145—146 °C; yellow prisms; IR (KBr) 3250, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.33, 7.90 (each 1H, d, PyH, J=8.4 Hz), 7.41—7.70 (15H, m), 8.93 (1H, broad, NH); MS m/z 382 (M^+). Found: C, 75.49; H, 4.65; N, 7.12%. Calcd for $C_{24}H_{18}N_2OS$: C, 75.36; H, 4.74; N, 7.33%.

2-Phenyl-3-phenylthiopyridine (21). i) From the Phenylcarbamoylpyridine (19). A suspension of 0.3 g (0.8 mmol)

of the pyridine (**19**) in an ethanolic potassium hydroxide solution, which was prepared from potassium hydroxide (0.5 g) in ethanol (20 ml), was refluxed for 3 h. The mixture was poured into water (20 ml) and extracted with benzene (20 ml×2). The aqueous layer was acidified with hydrochloric acid, and extracted with chloroform (30 ml×2). The chloroform extract was concentrated in vacuo to give 0.15 g (61%) of 6-phenyl-5-phenylthio-2-pyridinecarboxylic acid (**20**). After 0.2 g of the carboxylic acid (**20**) was heated at 230—250 °C for 15 min, the product was purified by chromatography (silica gel, benzene) to give 60 mg (35%) of the pyridine (**21**).

20: Mp 141—142 °C; colorless prisms; IR (KBr) 2800—3050, 1700 cm^{-1}; MS *m/z* 307 (M^+). Found: C, 70.51; H, 4.33; N, 4.44%. Calcd for $C_{18}H_{13}NO_2S$: C, 70.33; H, 4.26; N, 4.56%.

21: Oil; ^1H NMR ($CDCl_3$) δ=7.01 (1H, dd, PyH(β), J=4.8, 8.0 Hz), 7.39 (1H, dd, PyH(γ), J=1.2, 8.0 Hz), 7.20—7.55 (8H, m), 7.55—7.80 (2H, m), 8.45 (1H, dd, PyH(α), J=1.2, 4.8 Hz); MS *m/z* 263 (M^+). Found: C, 77.80; H, 4.68; N, 5.26%. Calcd for $C_{17}H_{13}NS$: C, 77.53; H, 4.98; N, 5.32%.

ii) From 6-Chloro-2-phenyl-3-phenylthiopyridine (8a). A solution of 0.23 g (0.8 mmol) of the chloropyridine (**8a**) in acetic acid (20 ml) was refluxed with zinc dust (1.5 g) for 8 h. The hot reaction mixture was filtered and the precipitate was washed with benzene (30 ml). The filtrate was poured into water (100 ml), and the resultant mixture was extracted with benzene (50 ml). The benzene extract was concentrated in vacuo and the residue was chromatographed (silica gel, benzene) to give 0.1 g (49%) of the pyridine (**21**).

6-Amino-2-phenyl-3-phenylthiopyridine (22). In a 10% ethanolic potassium hydroxide solution (20 ml) was heated 0.1 g of the (benzoylamino)pyridine (**11**) under reflux for 4 h. After the reaction mixture was concentrated in vacuo, the residue was triturated with water (10 ml), and then extracted with chloroform (30 ml). The extract was concentrated in vacuo, and the residue was chromatographed (silica gel, chloroform) to give 30 mg (41%) of the aminopyridine (**22**): Mp 177—178 °C; yellow needles; IR (KBr) 3460, 3300, 2950, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.66 (2H, broad, NH_2). 6.41, 7.52 (each 1H, d, PyH, J=8.4 Hz), 6.96—7.56 (10H, m); MS *m/z* 278 (M^+). Found: C, 73.20; H, 4.79; N, 9.80%. Cacld for $C_{17}H_{14}N_2S$: C, 73.35; H, 5.07; N, 10.06%.

6-Phenyl-5-phenylthio-2-pyridone (23). After diazotization of 0.1 g of the aminopyridine (**22**) with sodium nitrite (50 mg) in aqueous sulfuric acid (conc sulfuric acid (1 ml) and water (10 ml)) was carried out at 0—5 °C, the reaction mixture was heated at 50—60 °C for 1 h. Water (10 ml) was added to the mixture and the mixture was extracted with chloroform (20 ml×2). The extract was concentrated in vacuo, and the residue was chromatographed (silica gel, chloroform) to give 30 mg (30%) of the pyridone (**23**): Mp 206—208 °C; colorless needles; IR (KBr) 2700—3100, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.43 (1H, d, PyH, J=9.0 Hz), 7.00—7.60 (11H, m, ArH and PyH); MS *m/z* 279 (M^+). Found: C, 73.29; H, 4.41; N, 5.26%. Calcd for $C_{17}H_{13}NOS$: C, 73.10; H, 4.69; N, 5.01%.

Oxidation of the Pyridone (23). A solution of 0.1 g of the pyridone (**23**) in acetic acid (20 ml) was heated with 35% hydrogen peroxide (2 ml) under reflux for 3 h. The reaction mixture was concentrated in vacuo, and the residue was chromatographed (silica gel, chloroform–ethyl acetate (7:3)) to give 50 mg (45%) of the phenylsulfonylpyridone (**17**).

Thermolysis of the 4-(*p*-Methylphenylthio)-7-phenylthio-1,2-diazocine (6a). A solution of 0.73 g (1.5 mmol) of the 1,2-diazocine (**6a**) in dry xylene (20 ml) was refluxed for 5 h. The mixture was concentrated in vacuo, and the residue was chromatographed (silica gel, benzene) to give 0.12 g (78%) of benzonitrile and 0.39 g (63%) of a mixture of 6-(*p*-methylphenylthio)-2-phenyl-3-phenylthio- (**24a**) and 3-(*p*-methylphenylthio)-2-phenyl-6-phenylthiopyridine (**25a**) whose ratio was found to be 1:1 on the basis of ^1H NMR spectrum (δ=2.28, 2.34 (each s, CH_3)). It was very difficult to isolate pure **24a** and **25a** from the mixture.

Oxidation of the Mixture of 24a and 25a. A 6.6% aqueous potassium permanganate solution was slowly added, at room temperature, to a stirred solution of 0.17 g (0.4 mmol) of the mixture of **24a** and **25a** in acetic acid (30 ml); when about 6 ml of the permanganate solution was added, reddish violet color of the reaction mixture did not disappear. After a 10% aqueous sodium hydrogensulfite solution (12 ml) was added to the reaction mixture, the resultant clear solution was poured into water (50 ml) to give 0.14 g (71%) of a 1:1 mixture of 6-(*p*-methylphenylsulfonyl)-2-phenyl-3-phenylsulfonyl- (**26a**) and 3-(*p*-methylphenylsulfonyl)-2-phenyl-6-phenylsulfonylpyridine (**27a**): Mp 171—176 °C; ^1H NMR ($CDCl_3$) δ=2.29, 2.37 (each s, CH_3, relative intensity 1:1). Again it was very difficult to isolate pure **26a** and **27a** from the mixture.

Conversion of the Mixture of 26a and 27a into the Methoxypyridines 16a and 16b. In a solution of sodium methoxide in methanol, which was prepared from metallic sodium (0.5 g) in methanol (30 ml), 0.14 g (0.3 mmol) of the mixture of **26a** and **27a** was heated under reflux for 5 h. The reaction mixture was poured into water (50 ml), and the mixture was extracted with benzene (50 ml×2). The extract was concentrated in vacuo, and the residue was chromatographed (silica gel, benzene) to give 30 mg (30%) of 6-methoxy-2-phenyl-3-phenylsulfonylpyridine (**16a**) and 40 mg (36%) of 6-methoxy-3-(*p*-methylphenylsulfonyl)-2-phenylpyridine (**16b**), respectively.

Thermolysis of 4-(*p*-Chlorophenylthio)-7-phenylthio-1,2-diazocine (6b). A solution of 0.69 g (1.4 mmol) of the 1,2-diazocine (**6b**) in dry xylene (20 ml) was refluxed for 5 h. Similar work-up and chromatography (silica gel, benzene) of the residue gave 0.13 g (76%) of benzonitrile and 0.46 g (84%) of a mixture of 6-(*p*-chlorophenylthio)-2-phenyl-3-phenylthio- (**24b**) and 3-(*p*-chlorophenylthio)-2-phenyl-6-phenylthiopyridine (**25b**). Since it was very difficult to isolate pure **24b** and **25b**, the mixture was subjected to oxidation. A similar oxidation of 0.27 g of the mixture of **24b** and **25b** with potassium permanganate in acetic acid gave 0.14 g (45%) of 6-(*p*-chlorophenylsulfonyl)-2-phenyl-3-phenylsulfonylpyridine (**26b**) and 70 mg (23%) of 3-(*p*-chlorophenylsulfonyl)-2-phenyl-6-phenylsulfonylpyridine (**27b**), respectively.

26b: Mp 183—185 °C; colorless needles; IR (KBr) 1325 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.00—7.60 (6H, m), 7.80—8.10 (2H, m), 8.29, 8.86 (each 1H, d, PyH, J=8.4 Hz); MS *m/z* 407, 405 (M^+-SO_2). Found: C, 58.82; H, 3.58; N, 3.10%. Calcd for $C_{23}H_{16}NO_4S_2Cl$: C, 58.78; H, 3.43; N, 2.98%.

The sulfonylpyridines **26b** and **27b** reacted with sodium methoxide in methanol to give the methoxypyridines **16a** and **16c**, respectively.

Thermolysis of the 4-Acetoxy-7-phenylthio-1,2-diazocine

(7). A solution of 1.0 g (2.4 mmol) of the 1,2-diazocine (**7**) in dry xylene (20 ml) was refluxed for 5 h. Similar work-up and chromatography (silica gel, benzene) of the residue gave 0.17 g (69%) of benzonitrile and 0.66 g (87%) of 6-acetoxy-2-phenyl-3-phenylthiopyridine (**28**).

28: Oil; IR (neat) 1760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.30 (3H, s), 6.87, 7.45 (each 1H, d, PyH, J=7.8 Hz), 7.20—7.70 (10H, m); MS m/z 321 (M^+). Found: C, 71.23; H, 4.66; N, 4.23%. Calcd for $C_{19}H_{15}NO_2S$: C, 71.00; H, 4.70; N, 4.36%.

Hydrolysis of the Acetoxypyridine (28) to the Pyridone (23). A solution of 0.5 g (1.6 mmol) of the pyridine (**28**) in an ethanolic alkali solution (sodium hydrogencarbonate (1.0 g) in ethanol (50 ml)) was refluxed for 4 h. After the mixture was concentrated in vacuo, the residue was triturated with water (30 ml), and extracted with chloroform (30 ml×2). The extract was concentrated in vacuo, and the residue was chromatographed (silica gel, chloroform) to give 0.27 g (62%) of the pyridone (**23**).

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