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

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Nucleophilic substitution of 4,7-dichloro-3,8-diphenyl-1,2-diazocine with benzenesulfinate gave stable 7-chloro-4-phenylsulfonyl- and 4,7-bis(phenylsulfonyl)-1,2-diazocine. The 4-mono(arylsulfonyl)- and 4,7-bis-(arylsulfonyl)-1,2-diazocines were obtained by oxidation of the corresponding mono(arylthio)- and bis(arylthio)-1,2-diazocines, respectively. 4-Phenylsulfonyl-7-phenylthio-1,2-diazocine was also prepared. Thermolysis of all the diazocines gave only pyridine derivatives, and the feature of the thermolysis was also described.

Although Trost et al.[1] succeeded in an elegant synthesis of 1,2-diazacycloocta-2,4,6,8-tetraene, the parent 1,2-diazocine, substituted monocyclic 1,2-diazocines were not known until we reported the synthesis of stable 4,7-disubstituted 3,8-diphenyl-1,2-diazocines: 4,7-Dichloro-3,8-diphenyl-1,2-diazocine (**1**),[2] which can be readily obtained through a chlorination–dehydrochlorination sequence starting from 3,8-diphenyl-1,2-diazacycloocta-2,8-diene,[3] reacted with nucleophiles such as carboxylate anions[2] and arenethiols[4] to give the corresponding 4-substituted and 4,7-disubstituted 1,2-diazocines. In addition, it has been found that in contrast to the parent 1,2-diazocine, which decomposed slowly in solution at room temperature and rapidly neat to benzene and pyridine with comparable rates,[1] thermolysis of these stable 1,2-diazocines in refluxing toluene or xylene gave only pyridines with the extrusion of benzonitrile. This provided a new route for the synthesis of 3,6-disubstituted 2-phenylpyridines.

In order to obtain further information on thermal behavior of stable 1,2-diazocines, we have investigated the preparation of 1,2-diazocines bearing electron-withdrawing arenesulfonyl groups in place of electron-donating groups such as acyloxy[2] and arylthio groups,[4] and their thermolysis.

Results and Discussion

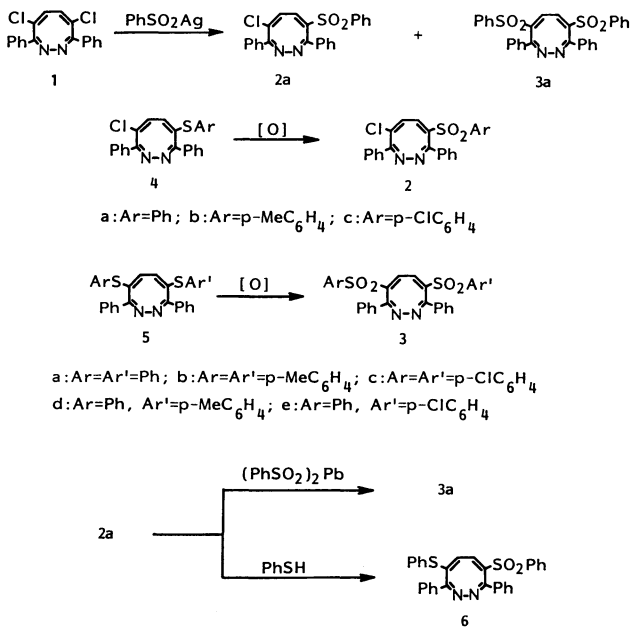
Preparation of Arylsulfonyl-Substituted 1,2-Diazocines. As expected, the dichloro-1,2-diazocine (**1**) reacted with two equivalents of silver benzenesulfinate in benzene under reflux for 6 h to give 7-chloro-3,8-diphenyl-4-phenylsulfonyl- (**2a**) and 4,7-bis(phenylsulfonyl)-3,8-diphenyl-1,2-diazocine (**3a**) in 83 and 3% yields, respectively. It has been found, however, that oxidations of the 4-arylthio-7-chloro- (**4a—c**)[4] and 4,7-bis(arylthio)-1,2-diazocines (**5a—e**)[4] with potassium permanganate or hydrogen peroxide in acetic acid afforded the corresponding mono(arylsulfonyl)-, **2a—c**, and bis(arylsulfonyl)-1,2-diazocines, **3a—e**, in fairly good yields, respectively (Scheme 1).

On the other hand, 3,8-diphenyl-4-phenylsulfonyl-7-phenylthio-1,2-diazocine (**6**) was obtained from the reaction of the mono(phenylsulfonyl)-1,2-diazocine (**2a**) with benzenethiol or the reaction of the mono(phenylthio)-1,2-diazocine (**4a**) with lead benzenesulfinate in benzene under reflux, respectively.

Structural elucidation of all the 1,2-diazocines, **2**, **3**, and **6**, was accomplished on the basis of spectral data.

Thermolysis of Arylsulfonyl-Substituted 1,2-Diazocines. We have first investigated the thermolysis of the mono(arylsulfonyl)-1,2-diazocines (**2**). When a solution of the phenylsulfonyl-1,2-diazocine (**2a**) in dry xylene was heated under reflux for 5 h, three pyridines, 3-chloro-2-phenyl-6-phenylsulfonyl- (**7a**), 6-benzoyl-2-phenyl-3-phenylsulfonyl- (**8a**), and 6-benzoyl-3-chloro-2-phenylpyridine (**9**) were isolated together with benzonitrile in small amounts.

Thermolysis of the (*p*-tolylsulfonyl)- (**2b**) and (*p*-chlorophenylsulfonyl)-1,2-diazocine (**2c**) under simi-



Scheme 1.

lar conditions gave the corresponding 6-arylsulfonyl-3-chloro-2-phenyl- (**7b** and **7c**), 3-arylsulfonyl-6-benzoyl-2-phenylpyridines (**8b** and **8c**) and the pyridine **9**, accompanied by trace amounts of benzonitrile, respectively (Scheme 2).

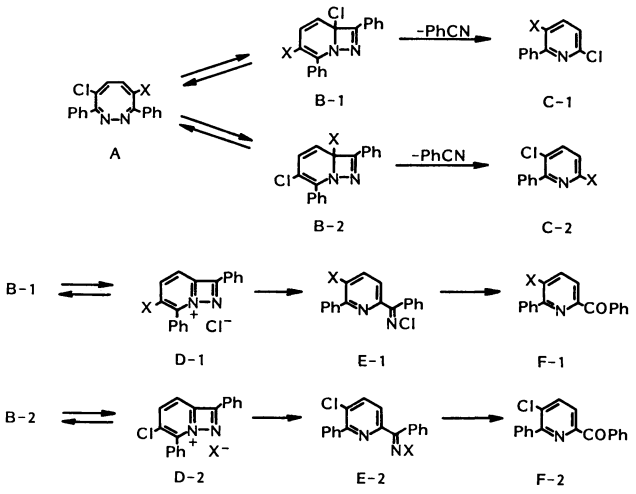
The structures of the pyridines, **7** and **8**, were confirmed on the basis of spectral data. In addition, the reaction of the pyridines, **7a—c**, with sodium methoxide in methanol afforded the same product, 3-chloro-6-methoxy-2-phenylpyridine (**10**), which was identical with an authentic sample prepared from 3,6-dichloro-2-phenylpyridine (**11**).[2] The pyridine **8a** was also obtained by the oxidation of 6-benzoyl-2-phenyl-3-phenylthiopyridine (**12**).[4] The pyridine **9** was identical with the product obtained from the thermolysis of the dichloro-1,2-diazocine (**1**) in wet toluene under reflux.[2]

As reported previously,[2,4] 4,7-disubstituted 3,8-diphenyl-1,2-diazocines are thermally isomerized into their valence isomers, diazabicyclooctatrienes. In the case of unsymmetrically 4,7-disubstituted 1,2-diazocines **A**, two valence isomers, **B-1** and **B-2**, are possible. 4-Acyloxy-7-chloro-[2] and 4-arylthio-7-chloro-1,2-diazocines[4] are exclusivly isomerized into their valence isomers **B-1** (X=OCOR and SAr), which decomposed into the corresponding 6-chloropyridines **C-1** (X=OCOR and SAr) with the extrusion of benzonitrile, respectively (Scheme 3).

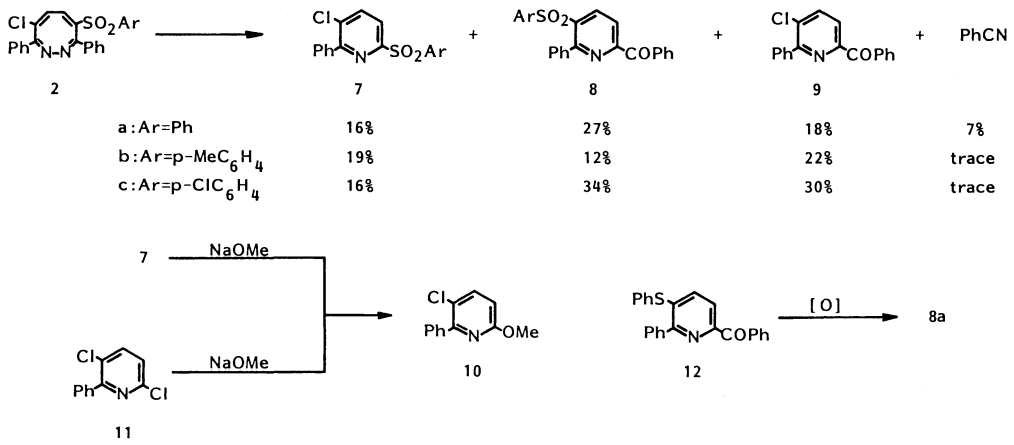
As illustrated in Scheme 2, however, the mode of decomposition of the arylsulfonyl-substituted 1,2-diazocines (**2**) is somewhat different from those of the acyloxy- and arylthio-substituted 1,2-diazocines. The 1,2-diazocines **2** seem to be preferentially isomerized into **B-2** (X=SO_2Ar) rather than **B-1** (X=SO_2Ar). It is evident that the pyridines, **7** and **9**, are derived from the **B-2**: The extrusion of benzonitrile from the **B-2** gives the pyridines **7**, and the pyridine **9** corresponds to the hydrolytic compounds **F-2** (X=SO_2Ar) of the imidoylpyridines **E-2** (X=SO_2Ar) arising from ring opening of the azonia intermediates **D-2** (X=SO_2Ar).[5]

In analogy with the formation of **9**, the pyridines **8** form via the processes, **B-1**→**D-1**→**E-1**→**F-1** (each X=SO_2Ar) (Scheme 3). Taking into account the formation of the pyridines, **8** and **9**, it should be emphasized that the arenesulfonyl group suppresses the extrusion of benzonitrile from the valence isomers, **B-1** and **B-2**, respectively.

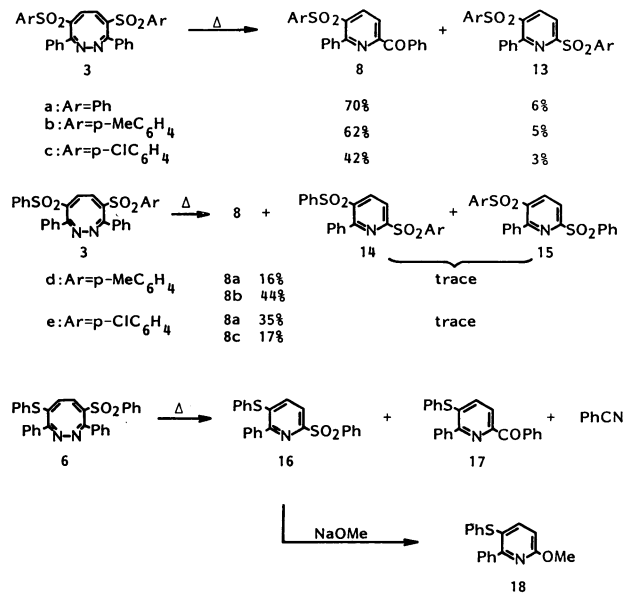
Next, the thermolysis of the bis(arylsulfonyl)-1,2-diazocines (**3**) was carried out under similar conditions. The symmetrical bis(arylsulfonyl)-1,2-diazocines (**3a—c**) gave the corresponding 3-arylsulfonyl-6-benzoyl-2-phenylpyridines (**8a—c**) as the main products, together with small amounts of the corresponding 3,6-bis(arylsulfonyl)-2-phenylpyridines (**13a—c**),[4] respectively (Scheme 4). In the thermolysis of the unsymmetrical bis(arylsulfonyl)-1,2-diazocine (**3d** or **3e**), two 3-arylsulfonyl-6-benzoyl-2-phenylpyridines (**8a** and **8b**) or (**8a** and **8c**) were obtained together with trace amounts of a mixture of the corresponding 6-arylsulfonyl-2-phenyl-3-phenylsulfonyl- (**14**) and 3-arylsulfonyl-2-phenyl-6-phenylsulfonylpyridine (**15**), respectively.



Scheme 3.

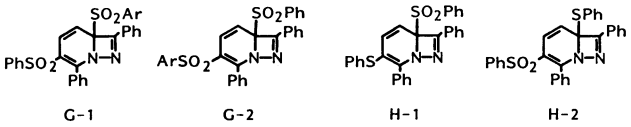


Scheme 2.



Scheme 4.

When the 4-phenylsulfonyl-7-phenylthio-1,2-diazocine (**6**) was pyrolyzed under similar conditions, 2-phenyl-6-phenylsulfonyl-3-phenylthio- (**16**) and 6-benzoyl-2-phenyl-3-phenylthiopyridine (**17**)[4] were obtained together with benzonitrile. The pyridine **16** was converted into 6-methoxy-2-phenyl-3-phenylthiopyridine (**18**)[4] (Scheme 4).



On the basis of the results shown in Scheme 4, it is clear that the unsymmetrical bis(arylsulfonyl)-1,2-diazocines (**3d** and **3e**) decomposed via two possible valence isomers, **G-1** and **G-2**. However, the decomposition of **3d** occurs somewhat more preferentially via **G-2** than **G-1**, and the reverse in **3e**. On the other hand, the 1,2-diazocine **6** exclusively decomposes via **H-1**, but not **H-2**.

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. Elementary analyses were performed on a Yanaco MT 2 CHN corder instrument.

Reaction of the Dichloro-1,2-diazocine (1) with Silver Benzenesulfinate. A solution of the diazocine **1**[2] (1.3 g, 4mmol) in benzene (50 ml) was refluxed with silver benzenesulfinate (2.0 g, 8 mmol) for 6 h. The reaction mixture was filtered, and the precipitate was washed with benzene (50 ml). The combined benzene solution was concentrated in vacuo, and the residue was chromatographed on silica gel to give 1.42 g (83%) of the mono(phenylsulfonyl)-1,2-diazocine (**2a**) (from benzene elution) and 60 mg (3%) of the bis(phenylsulfonyl)-1,2-diazocine (**3a**).

2a: Mp 180—181 °C (decomp); colorless needles; IR (KBr) 1320 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.60 (1H, d, =CH, J=4.2 Hz), 7.20—7.80 (16H, m, =CH and ArH); ^{13}C NMR ($CDCl_3$) δ=149.29, 148.36, 142.61, 141.61, 139.90, 133.86, 132.21 (each s), 131.22, 130.63, 130.16, 128.58, 128.39, 128.11, 127.69; MS m/z 434, 432 (M^+). Found: C, 66.58; H, 3.87; N, 6.38%. Calcd for $C_{24}H_{17}N_2O_2SCl$: C, 66.58; H, 3.96; N, 6.47%.

3a: Mp 227—229 °C (decomp); colorless needles; IR (KBr) 1320 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.75 (2H, s, =CH), 7.40—7.70 (20H, m); MS m/z 538 (M^+). Found: C, 66.83; H, 4.05; N, 5.42%. Calcd for $C_{30}H_{22}N_2O_4S_2$: C, 66.89; H, 4.12; N, 5.20%.

Oxidation of the 4-Arylthio-7-chloro-1,2-diazocines (4). Typical run is illustrated for the phenylthiodiazocine **4a**.

i) With Hydrogen Peroxide: A solution of 0.8 g (2 mmol) of **4a**[4] in acetic acid (30 ml) was refluxed with 35% hydrogen peroxide (10 ml) for 1.5 h. The reaction mixture was poured into water (50 ml) to precipitate solid, which on recrystallization from benzene gave 0.52 g (60%) of the mono(phenylsulfonyl)-1,2-diazocine (**2a**).

ii) With Potassium Permanganate. A 6.6% aqueous potassium permanganate solution was slowly added, at room temperature, to a stirred solution of 0.8 g (2 mmol) of **4a** in acetic acid (40 ml); when about 8 ml of the permanganate solution was added, reddish violet color of the reaction mixture did not disappear. After a 10% aqueous sodium hydrogensulfite solution (18 ml) was added to the reaction mixture, the resultant clear solution was poured into water (50 ml) to give 0.5 g (58%) of **2a**.

Similar oxidations of the 4-chloro-7-(*p*-methylphenylthio)- (**4b**)[4] and 4-chloro-7-(*p*-chlorophenylthio)-1,2-diazocine (**4c**)[4] with potassium permanganate in acetic acid gave the corresponding mono(arylsulfonyl)-1,2-diazocines **2b** and **2c** in 50 and 58% yields, respectively.

2b: Mp 186—188 °C (decomp); colorless needles; IR (KBr) 1320 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.32 (3H, s), 6.67 (1H, d, =CH, J=4.2 Hz), 6.98—7.80 (15H, m, =CH and ArH); MS m/z 449, 446 (M^+). Found: C, 67.29; H, 4.01; N, 6.16%. Calcd for $C_{25}H_{19}N_2O_2SCl$: C, 67.18; H, 4.29; N, 6.27%.

2c: Mp 177—179 °C (decomp); colorless needles; IR (KBr) 1330 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.64 (1H, d, =CH, J=4.2 Hz), 7.01—7.71 (15H, m, =CH and ArH); MS m/z 470, 468, 466 (M^+). Found: C, 61.80; H, 3.61; N, 5.76%. Calcd for $C_{24}H_{16}N_2O_2SCl_2$: C, 61.67; H, 3.45; N, 5.99%.

Oxidation of the 4,7-Bis(arylthio)-1,2-diazocines (5). Typical run is illustrated for the bis(phenylthio)diazocine **5a**.

i) With Hydrogen Peroxide. A solution of 0.95 g (2 mmol) of **5a**[4] in acetic acid (30 ml) was refluxed with 35% hydrogen peroxide (10 ml) for 1.5 h. The reaction mixture was poured into water (50 ml) to precipitate solid, which on recrystallization from petroleum ether gave 0.68 g (63%) of the bis(phenylsulfonyl)-1,2-diazocine (**3a**).

ii) With Potassium Permanganate. To a stirred solution of **5a** (0.5 g, 1 mmol) in acetic acid (40 ml), a 6.6%

aqueous potassium permanganate solution was slowly added at room temperature; 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 0.41 g (76%) of **3a**.

Similar oxidations of the bis(*p*-methylphenylthio)- (**5b**)[4] and bis(*p*-chlorophenylthio)-1,2-diazocine (**5c**)[4] with potas sium permanganate in acetic acid gave the bis(*p*-tolylsulfonyl)- (**3b**) and bis(*p*-chlorophenylsulfonyl)-1,2-diazocine (**3c**) in 62 and 53% yields, respectively.

3b: Mp 245—247 °C (decomp); colorless needles; IR (KBr) 1320 cm^{-1}; MS *m/z* 566 (M^+). Found: C, 68.15; H, 4.50; N, 4.91%. Calcd for $C_{32}H_{26}N_2O_4S_2$: C, 67.82; H, 4.62; N, 4.94%.

3c: Mp 173—174 °C (decomp); colorless needles; IR (KBr) 1330 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.64 (2H, s, =CH), 7.02—7.57 (18H, m); MS *m/z* 610, 608, 606 (M^+). Found: C, 59.53; H, 3.11; N, 4.86%. Calcd for $C_{30}H_{20}N_2O_4S_2Cl_2$: C, 59.31; H, 3.32; N, 4.61%.

4-Phenylsulfonyl-7-phenylthio-1,2-diazocine (6). i) A solution of 0.58 g (1.3 mmol) of the mono(phenylsulfonyl)-1,2-diazocine (**2a**) in benzene (30 ml) was refluxed with 0.33 g (3 mmol) of benzenethiol for 4 h. After the reaction mixture was washed with a 10% aqueous sodium hydroxide solution and then water, the benzene solution was concentrated in vacuo to leave the residue. Chromatography (silica gel, benzene) of the residue gave 0.45 g (78%) of unreacted **2a** and 0.14 g(21%) of the 1,2-diazocine **6**.

ii) A solution of 0.8 g (2 mmol) of the phenylthiodiazocine **4a** in benzene (50 ml) was heated with 1.0 g (2 mmol) of lead benzenesulfinate under reflux for 18 h. The reaction mixture was filtered, and the precipitate was washed with benzene (30 ml). The combined benzene solution was concentrated in vacuo, and chromatography (silica gel, benzene) of the residue afforded 0.17 g (21%) of unreacted **4a** and 0.52 g (51%) of **6**.

6: Mp 203—204 °C (decomp); colorless needles; IR (KBr) 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.20 (1H, d, =CH, *J*=4.2 Hz), 7.01—7.81 (21H, m, -CH and ArH); MS *m/z* 506 (M^+). Found: C, 69.97; H, 4.09; N, 5.75%. Calcd for $C_{30}H_{22}N_2O_2S_2$: C, 71.12; H, 4.38; N, 5.53%.

Thermolysis of the 7-Chloro-4-phenylsulfonyl-1,2-diazocine (2a). A solution of 1.0 g (2.3 mmol) of **2a** in dry xylene (20 ml) was refluxed for 5h. The reaction mixture was concentrated in vacuo, and the residue was chromatographed (silica gel, benzene) to give 20 mg (7%) of benzonitrile, 0.12 g (16%) of 3-chloro-2-phenyl-6-phenylsulfonylpyridine (**7a**), 0.25 g (27%) of 6-benzoyl-2-phenyl-3-phenylsulfonylpyridine (**8a**), and 0.12 g (18%) of 6-benzoyl-3-chloro-2-phenylpyridine (**9**), mp 119—120 °C (lit.[2] mp 119—120 °C).

7a: Mp 132—133 °C; yellow prisms; IR (KBr) 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.97, 8.05 (each 1H, d, PyH, *J*=8.4 Hz), 7.32—7.82 (8H, m), 7.97—8.22 (2H, m); ^{13}C NMR ($CDCl_3$) δ=156.98, 156.46, 139.50, 138.61, 136.33, 133.86, 133.63, 129.57, 129.58, 129.05, 127.99, 121.06; MS *m/z* 267, 265 (M^+-SO_2). Found: C, 61.82; H, 3.56; N, 4.07%. Calcd for $C_{17}H_{12}NO_2SCl$: C, 61.91; H, 3.67; N, 4.25%.

8a: Mp 159—160 °C; yellow needles; IR (KBr) 1665, 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.11, 8.86 (each 1H, d, PyH, *J*=8.2 Hz), 7.10—7.60 (13H, m), 7.97—8.12 (2H, m); ^{13}C NMR ($CDCl_3$) δ=191.87, 157.81, 157.40, 139.14, 138.88, 138.20, 137.15, 135.09, 133.39, 133.16, 130.98, 129.63, 128.87, 128.52, 128.16, 127.87, 127.45, 122.70; MS *m/z* 399 (M^+). Found: C, 71.95; H, 4.51; N, 3.65%. Calcd for $C_{24}H_{17}NO_3S$: C, 72.16; H, 4.29; N, 3.51%.

Thermolysis of the 4-Chloro-7-(*p*-tolylsulfonyl)-1,2-diazocine (2b). A solution of 0.7 g (1.6 mmol) of **2b** in dry xylene (20 ml) was refluxed for 5h. Similar work-up and chromatography (silica gel, benzene) of the pyrolysate gave trace amounts of benzonitrile, 0.1 g (19%) of 3-chloro-2-phenyl-6-(*p*-tolylsulfonyl)pyridine (**7b**), 80 mg (12%) of 6-benzoyl-2-phenyl-3-(*p*-tolylsulfonyl)pyridine (**8b**), and 0.1 g (22%) of the pyridine **9**.

7b: 142—143 °C; colorless needles; IR (KBr) 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.40 (3H, s), 7.33—7.83 (8H, m, PyH and ArH) 7.83—8.13 (3H, m, PyH and ArH); MS *m/z* 281, 279 (M^+-SO_2). Found: C, 63.01; H, 4.26; N, 4.33%. Calcd for $C_{18}H_{14}NO_2SCl$: C, 62.88; H, 4.10; N, 4.07%.

8b: Mp 163—164 °C; colorless prisms; IR (KBr) 1655, 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.33 (3H, s), 8.06, 8.81 (each 1H, d, PyH, *J*=8.4 Hz), 6.76—7.56 (12H, m), 7.86—8.16 (2H, m): MS *m/z* 413 (M^+). Found: C, 72.37; H, 4.50; N, 3.43%. Calcd for $C_{25}H_{19}NO_3S$: C, 72.62; H, 4.63; N, 3.39%.

Thermolysis of the 4-Chloro-7-(*p*-chlorophenylsulfonyl)-1,2diazocine (2c). A solution of 0.8 g (1.7 mmol) of **2c** in dry xylene (20 ml) was refluxed for 5 h. Similar work-up and chromatography (silica gel, benzene) of the pyrolysate gave trace amounts of benzonitrile, 0.1 g (16%) of 3-chloro-6-(*p*-chlorophenylsulfonyl)-2-phenylpyridine (**7c**), 0.25 g (34%) of 6-benzoyl-3-(*p*-chlorophenylsulfonyl)-2-phenylpyridine (**8c**), and 0.15 g (30%) of the pyridine **9**.

7c: Mp 132—133 °C; colorless needles; IR (KBr) 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.29—7.69 (8H, m, PyH and ArH), 7.94—8.19 (3H, m, PyH and ArH); MS *m/z* 303, 301, 299 (M^+-SO_2). Found: C, 56.06; H, 3.04; N, 3.85%. Calcd for $C_{17}H_{11}NO_2SCl_2$: C, 55.77; H, 3.21; N, 3.69%.

8c: Mp 147—148 °C; colorless needles; IR (KBr) 1660, 1330 cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.13, 8.85 (each 1H, d, PyH, *J*=8.4 Hz), 7.09—7.59 (12H, m), 7.78—8.19 (2H, m); MS *m/z* 435, 433 (M^+). Found: C, 66.21; H, 3.60; N, 3.49%. Calcd for $C_{24}H_{18}NO_3SCl$: C, 66.43; H, 3.72; N, 3.23%.

Conversion of the 3-Chloro-2-phenyl-6-phenylsulfonylpyridine (7a) to 3-Chloro-6-methoxy-2-phenylpyridine (10). The pyridine **7a** (0.2 g, 0.6 mmol) was heated in a solution of sodium methoxide in methanol, which was prepared from metallic sodium (0.5 g) in methanol (20 ml), 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 benzene extract was concentrated in vacuo, and chromatography (silica gel, benzene) of the residue gave 0.1 g (76%) of the pyridine **10**.

10: Oil; ^1H NMR ($CDCl_3$) δ=3.89 (3H, s), 6.59, 7.52 (each 1H, d, PyH, *J*=8.4 Hz), 7.27—7.52 (3H, m), 7.67—7.87 (2H, m); MS *m/z* 221, 219 (M^+). Found: C, 65.37; H, 4.62; N, 6.51%. Calcd for $C_{12}H_{10}NOCl$: C, 65.61; H, 4.59; N, 6.38%.

Similar treatments of 3-chloro-2-phenyl-6-(*p*-tolylsulfonyl)- (**7b**) and 3-chloro-6-(*p*-chlorophenylsulfonyl)-2-phenylpyridine (**7c**) with sodium methoxide in methanol afforded the pyridine **10** in 67 and 50% yields, respectively. The pyridine **10** was identical with the product from the reaction of 3,6-dichloro-2-phenylpyridine (**11**)[2] with sodium

methoxide in methanol under similar conditions.

Thermolysis of the Symmetrical Bis(arylsulfonyl)-1,2-diazocines. Typical run is illustrated for the bis(phenylsulfonyl)-1,2-diazocine (**3a**). A solution of **3a** (1.0 g, 1.9 mmol) in dry xylene (20 ml) was refluxed for 5 h. The reaction mixture was concentrated in vacuo, and the residue was chromatographed on silica gel to give 0.52 g (70%) of the pyridine **8a** (from benzene elution) and 50 mg (6%) of 3,6-bis(phenylsulfonyl)-2-phenylpyridine (**13a**), mp 187—189 °C (lit,[4] mp 187—189 °C) (from chloroform elution).

Thermolysis of the bis(*p*-tolylsulfonyl)- (**3b**) or bis(*p*-chlorophenylsulfonyl)-1,2-diazocine (**3c**) in dry xylene under similar conditions gave the pyridine **8b** and 3,6-bis(*p*-tolylsulfonyl)-2-phenylpyridine (**13b**), mp 231—232 °C (lit,[4] mp 231—232 °C), or the pyridine **8c** and 3,6-bis(*p*-chlorophenylsulfonyl)-2-phenylpyridine (**13c**), mp 227—228 °C (lit,[4] mp 227—228 °C), respectively. The results are shown in Scheme 4.

Thermolysis of the Unsymmetrical Bis(arylsulfonyl)-1,2-diazocines. A solution of 0.7 g (1.3 mmol) of the 4-phenylsulfonyl-7-(*p*-tolylsulfonyl)-1,2-diazocine (**3d**) in dry xylene (20 ml) was refluxed for 5 h. The reaction mixture was concentrated in vacuo, and the pyrolysate was chromatographed on silica gel to give 80 mg (16%) of **8a** and 0.23 g (44%) of **8b** (each from benzene elution), together with 10 mg of a mixture of 2-phenyl-3-phenylsulfonyl-6-(*p*-tolylsulfonyl)- (**14**) and 2-phenyl-6-phenylsulfonyl-3-(*p*-tolylsulfonyl)pyridine (**15**) (each Ar=*p*-MeC_6H_4) (from chloroform elution) whose ratio was not determined.

In the thermolysis of the 7-(*p*-chlorophenylsulfonyl)-4-phenylsulfonyl-1,2-diazocine (**3e**) under similar thermolytic conditions, two benzoylpyridines, **8a** and **8c**, were obtained accompanied by small amounts of a mixture of two the corresponding 3,6-bis(arylsulfonyl)-2-phenylpyridines, **14** and **15** (Ar=*p*-ClC_6H_4). whose ratio was not determined (See Scheme 4).

Thermolysis of the 4-Phenylsulfonyl-7-phenylthio-1,2-diazocine (6). A solution of **6** (0.6 g, 1.2 mmol) in dry xylene (20 ml) was refluxed for 5 h. Similar work-up and chromatography (silica gel, benzene) of the pyrolysate gave 60 mg (49%) of benzonitrile, 0.3 g (63%) of 2-phenyl-6-phenylsulfonyl-3-phenylthiopyridine (**16**), and 0.1 g (23%) of 6-benzoyl-2-phenyl-3-phenylthiopyridine (**17**), mp 120—121 °C (lit,[4] mp 120—121 °C). The pyridine **16** was converted into 6-methoxy-2-phenyl-3-phenylthiopyridine (**18**), mp 68—69 °C (lit,[4] mp 68—69 °C).

16: Mp 143—145 °C; colorless prisms; ^1H NMR ($CDCl_3$) δ=7.1—8.3 (m, PyH and ArH); MS *m/z* 399 (M^+-SO_2). Found: C, 68.17; H, 4.15; N, 3.67%. Calcd for $C_{23}H_{17}NO_2S_2$: C, 68.46; H, 4.25; N, 3.47%.

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5) The intervention of azonia intermediates like D and imidoylpyridines like **E** in the thermal reaction of 4,7-disubstituted 1,2-diazocines can be strongly supported by the isolation of 3-acetoxy-6-(*N*-chlorobenzimidoyl)-2-phenyl pyridine (Ref. 2).