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

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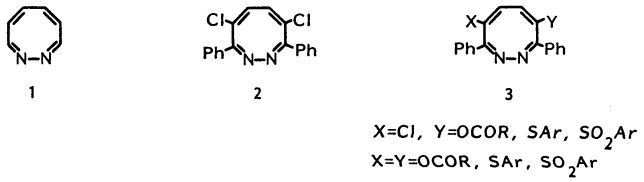
Nucleophilic substitution of 4,7-dichloro-3,8-diphenyl-1,2-diazocine with succinimide, phthalimide, *N*-methyl-*p*-toluenesulfonamide, and *o*-benzosulfimide, in the presence of silver oxide, gave the corresponding 4-mono(imido)- and 4,7-di(imido)-1,2-diazocines. 4-Acetoxy-7-phthalimido- and 4-phenylthio-7-phthalimido-1,2-diazocine were also prepared. Thermolysis of the mono(imido)-1,2-diazocines in xylene under reflux afforded the corresponding di(imido)-1,2-diazocine and/or five pyridine derivatives, whose relative yields depended upon the nature of imido substitutents in the diazocines. However, 4,7-di(imido)-1,2-diazocines did not decompose in xylene under reflux. Thermolysis of 4,7-bis(phthalimido)-1,2-diazocine at 300—310 °C gave 3,6-bis(phthalimido)-2-phenylpyridine with the extrusion of benzonitrile. In the thermolysis of the acetoxy- (230—240 °C) or phenylthio-substituted 1,2-diazocine (240—260 °C), 6-acetoxy- and 6-benzoyl-3-phthalimido-2-phenylpyridine, or 6(and 3)-phenylthio-3(and 6)-phthalimido-2-phenylpyridines were isolated together with benzonitrile, respectively. The feature of thermolysis was also discussed.

Although 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**), we have recently reported a convenient method for the synthesis of 4,7-dichloro-3,8-diphenyl-1,2-diazocine (**2**), which is the first example for stable substituted monocyclic 1,2-diazocine.[2] The 1,2-diazocine **2** can be readily converted into other 4,7-disubstituted 1,2-diazocines: Thus, stable acyloxy-,[2] arylthio-,[3] and arylsulfonyl-substituted[4] 1,2-diazocines **3** were prepared by the reaction of **2** with appropriate nucleophiles. It has also been found that in contrast to the parent 1,2-diazocine (**1**), which decomposed slowly in solution at room temperature and rapidly neat to benzene and pyridine with comparable rates,[1] these stable 1,2-diazocines, **2** and **3**, had been pyrolyzed to give only pyridines accompanied by the extrusion of benzonitrile in almost all cases.



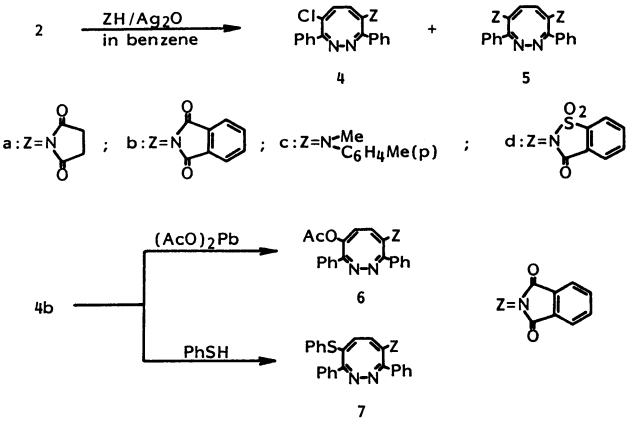
This paper describes the synthesis of stable imido-substituted 1,2-diazocines from **2**, and their thermolysis leading to pyridines. The feature of the thermolysis is also discussed.

Results and Discussion

Synthesis of Imido-Substituted 1,2-Diazocines. Although the dichloro-1,2-diazocine (**2**) did not react with succinimide in benzene under reflux, the reaction of **2** with silver succinimide (5 equiv) in benzene under reflux for 10 h afforded mono(succinimido)- **4a** and bis(succinimido)-1,2-diazocine **5a** in 39 and 34% yields, respectively. However, the succinimido-substituted 1,2-diazocines **4a** and **5a** could be also obtained in 41 and 11% yields respectively, together with unidentified viscous materials, by the reaction of **2** with succinimide (2 equiv) in the presence of silver oxide (2 equiv) in refluxing benzene for 6 h. This procedure was applied to the synthesis of other imido-substituted 1,2-diazocines.

The reaction of **2** with phthalimide, *N*-methyl-*p*-toluenesulfonamide, or *o*-benzosulfimide (saccharin) in the presence of silver oxide under the same conditions gave the corresponding mono(imido)-1,2-diazocines, **4b** (25%), **4c** (47%) or **4d** (47%), and di(imido)-1,2-diazocine, **5b** (36%), **5c** (16%), or **5d** (16%), respectively.

Moreover, in the reaction of mono(phthalimido)-1,2-diazocine (**4b**) with lead acetate or benzenethiol (each 3 equiv) in benzene under reflux for 20 or 10 h, 4-acetoxy-7-phthalimido-(**6**) or 4-phenylthio-7-phthalimido-1,2-diazocine (**7**) was obtained in 47 or 65% yield, respectively (Scheme 1).



Scheme 1.

Structural elucidation of all the imido-substituted 1,2-diazocines, **4**—**7**, was accomplished on the basis of spectral data.

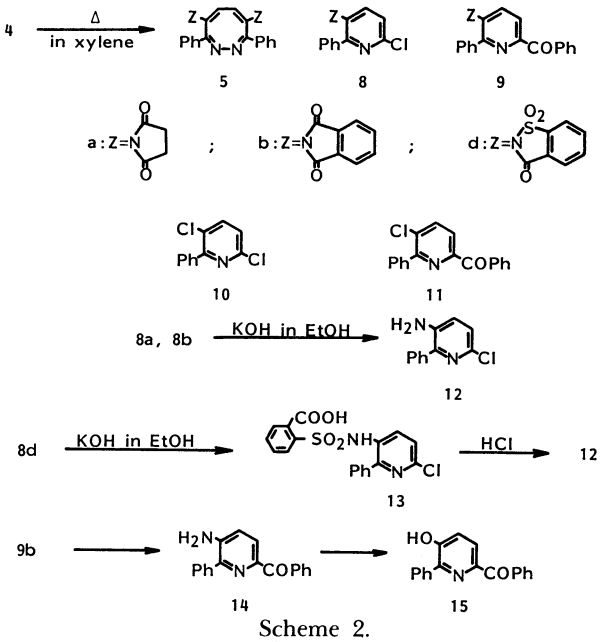
Thermolysis of Imido-Substituted 1,2-Diazocines. When the mono(succinimido)-1,2-diazocine (**4a**) was heated in dry xylene under reflux for 5 h, the bis-(succinimido)-1,2-diazocine (**5a**), 6-chloro-2-phenyl-

3-succinimidopyridine (**8a**) and 6-benzoyl-2-phenyl-3-succinimidopyridine (**9a**) were isolated in 35, 15, and 8% yields, respectively. The similar thermolysis of the mono(phthalimido)-1,2-diazocine (**4b**) gave 6-chloro-2-phenyl-3-phthalimidopyridine (**8b**) and 6-benzoyl-2-phenyl-3-phthalimidopyridine (**9b**) in 42 and 32% yields, respectively; in this case the bis(phthalimido)-1,2-diazocine (**5b**) was not formed, but benzonitrile was isolated in 17% yield.

The thermolysis of the mono(*N*-methyl-*p*-toluenesulfonamido) (**4c**) and mono(*o*-benzosulfimido)-1,2-diazocine (**4d**) was somewhat complex. The 1,2-diazocine **4c** gave only a complex mixture, from which any identified pyrolysates could not be isolated. In the thermolysis of **4d** under similar conditions, however, the bis(*o*-benzosulfimido)-1,2-diazocine (**5d**), 3-(*o*-benzosulfimido)-6-chloro-2-phenylpyridine (**8d**) and 6-benzoyl-3-(*o*-benzosulfimido)-2-phenylpyridine (**9d**) were isolated in 29, 9, and 11% yields respectively, together with 3,6-dichloro-2-phenylpyridine (**10**)[2] (17%) and 6-benzoyl-3-chloro-2-phenylpyridine (**11**)[2] (5%) (Scheme 2).

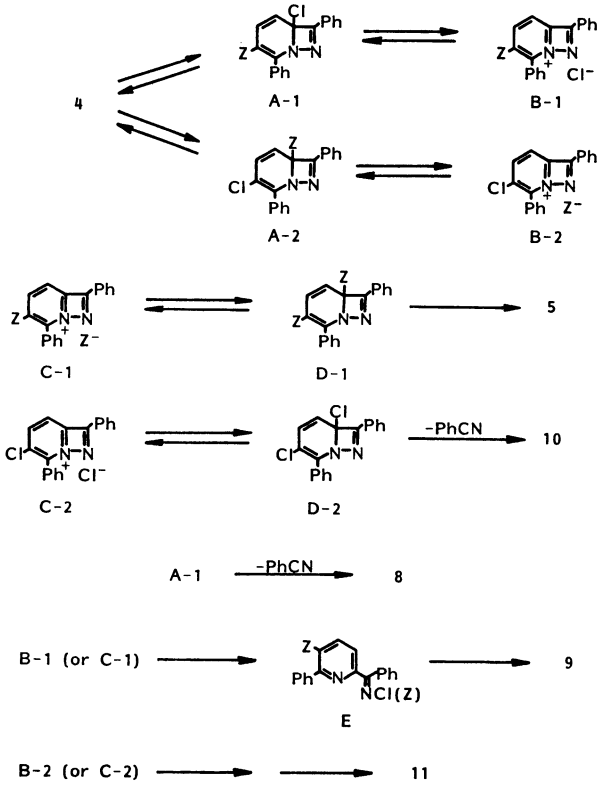
The structures of the pyridines, **8** and **9**, were assigned on the basis of spectral data as well as of the chemical conversions.

Treatment of the pyridines **8a** and **8b** with an ethanolic alkali solution under reflux gave the same product, 3-amino-6-chloro-2-phenylpyridine (**12**). The similar treatment of the pyridine **8d** gave an intermediary pyridine **13**, which was then converted into **12** on heating with hydrochloric acid. On the other hand, the treatment of **9b** with an ethanolic alkali solution under reflux afforded 3-amino-6-benzoyl-2-phenylpyridine (**14**), which was then converted, by diazotization, into known 6-benzoyl-3-hydroxy-2-phenylpyridine (**15**)[2] (Scheme 2).



Scheme 2.

As reported previously,[2-4] 4,7-disubstituted 1,2-diazocines, **2** and **3**, thermally isomerize into their valence isomers, diazabicyclooctatrienes, which are in equilibrium with azonia intermediates. Although thermolysis of the mono(imido)-1,2-diazocines (**4**) seemed somewhat more complex than that of the other stable 1,2-diazocines, **2** and **3**, the formation of products, **5** and **8**—**11**, in the thermolysis of **4** can be again explained by the intervention of diazabicyclooctatrienes and azonia intermediates (Scheme 3).



Scheme 3.

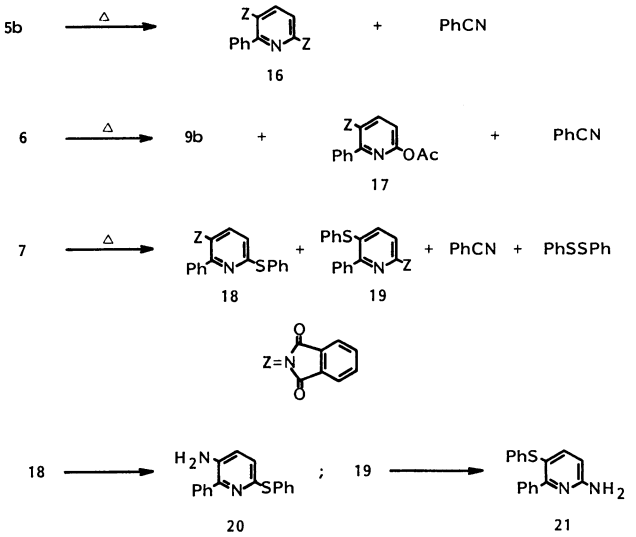
The 1,2-diazocine **4** is thermally isomerized into two valence isomers, **A-1** and **A-2**. The valence isomer **A-1** is in equilibrium with the azonia intermediate **B-1**, while **A-2** with **B-2**. The exchange of counter anion between **B-1** and **B-2** yields new azonia intermediates **C-1** and **C-2**, which are, of course, in equilibrium with the diazabicyclooctatrienes **D-1** and **D-2**, respectively. The pyridine **8** is formed from **A-1** with the extrusion of benzonitrile, whereas the ring opening of **B-1** (and/or **C-1**) to an imidoylpyridine **E**, followed by hydrolysis gives the pyridine **9**. The pyridines **10** and **11** are formed from **D-2** and **B-2** (and/or **C-2**) via similar processes, respectively. As mentioned below, di-(imido)-1,2-diazocines (**5**) are stable in xylene under reflux. Thus, **5** formed via a valence isomerization of **D-1** is unchanged under the conditions.

Next, thermolysis of 1,2-diazocines **5**—**7** was investigated. Since the 1,2-diazocines **5**—**7** did not decompose in xylene under reflux, thermolysis was performed without solvent. When the bis(phthalimido)-1,2-diazocine (**5b**) was heated at 300—310 °C (bath temp) for 15 min, benzonitrile and 3,6-bis(phthalimido)-2-phenylpyridine (**16**) were obtained in 43 and 20%

yields, respectively, together with unidentified viscous materials.

Thermolysis of the 4-acetoxy-7-phthalimido-1,2-diazocine (**6**) at 230—240 °C (bath temp) for 15 min gave the benzoylpyridine **9b** and 6-acetoxy-2-phenyl-3-phthalimidopyridine (**17**) in 11 and 10% yields respectively, together with traces of benzonitrile. When 4-phthalimido-7-phenylthio-1,2-diazocine (**7**) was heated at 240—260 °C (bath temp) for 15 min, 2-phenyl-6-phenylthio-3-phthalimidopyridine (**18**) and 2-phenyl-3-phenylthio-6-phthalimidopyridine (**19**) were isolated in 25 and 7% yields respectively, accompanied by benzonitrile (16%) and diphenyl disulfide (trace). Unidentified viscous materials were formed in thermolysis of **6** and **7**.

Structural elucidation of the pyridines **16**—**19** was accomplished on the basis of spectral data. Treatments of the pyridines **18** and **19** with an ethanolic alkali solution under reflux gave 3-amino-2-phenyl-6-phenylthiopyridine (**20**) and 6-amino-2-phenyl-3-phenylthiopyridine (**21**),[3] respectively (Scheme 4). The pathways for the thermolysis of the 1,2-diazocines **5**—**7** can be readily understood.



Scheme 4.

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 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 the Dichloro-1,2-diazocine (2) with Silver Succinimide. A mixture of **2** (0.65 g, 2.0 mmol) and silver succinimide (2.0 g, 10 mmol) in benzene (50 ml) was refluxed for 10 h. The reaction mixture was filtered, and the precipitate was washed with chloroform (50 ml). The combined filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel to give 0.30 g (39%) of 4-chloro-3,8-diphenyl-7-succinimido-1,2-diazocine (**4a**) (from benzene elution) and 0.30 g (34%) of 4,7-bis(succinimido)-3,8-diphenyl-1,2-diazocine (**5a**) (from chloroform elution).

4a: Mp 179—180 °C (decomp); colorless needles; IR (KBr) 1779, 1703, 1697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.51 (4H, s, CH_2), 6.68, 6.81 (each 1H, d, =CH, J=4.2 Hz), 7.2—7.6 (4H, m), 7.6—7.9 (4H, m); MS m/z 391, 389 (M^+). Found: C, 67.66; H, 4.01; N, 10.69%. Calcd for $C_{22}H_{16}N_3O_2Cl$: C, 67.78; H, 4.14; N, 10.78%.

5a: Mp 271—273 °C (decomp); colorless prisms; IR (KBr) 1778, 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.56 (8H, s, CH_2), 7.00 (2H, s, =CH), 7.1—7.6 (10 H, m); MS m/z 452 (M^+). Found: C, 69.23; H, 4.35; N, 12.24%. Calcd for $C_{26}H_{20}O_4N_4O_4$: C, 69.02; H, 4.46; N, 12.38%.

Reaction of the Dichloro-1,2-diazocine (2) with Succinimide in the Presence of Silver Oxide. A mixture of **2** (0.65 g, 2.0 mmol), succinimide (0.4 g, 4 mmol) and silver oxide (0.9 g, 4.0 mmol) in benzene (50 ml) was refluxed for 6 h. Similar work-up of the reaction mixture and chromatography of the residue on silica gel gave 0.32 g (41%) of the mono(succinimido)-1,2-diazocine (**4a**) (from benzene elution) and 0.1 g (11%) of the bis(succinimido)-1,2-diazocine (**5a**) (from chloroform elution), together with unidentified viscous materials (0.1 g).

Reaction of the Dichloro-1,2-diazocine (2) with Phthalimide in the Presence of Silver Oxide. A mixture of **2** (0.65 g, 2.0 mmol), phthalimide (0.6 g, 4 mmol) and silver oxide (0.9 g, 4.0 mmol) in benzene (50 ml) was refluxed for 3 h. Similar work-up of the reaction mixture and the residue was chromatographed on silica gel to give 0.19 g (29%) of unchanged **2**, 0.38 g (43%) of 4-chloro-3,8-diphenyl-7-phthalimido-1,2-diazocine (**4b**) (each from benzene elution), and 0.18 g (16%) of 4,7-bis(phthalimido)-3,8-diphenyl-1,2-diazocine (**5b**) (from chloroform elution).

The reaction for 6 h under similar conditions afforded 0.21 g (25%) of **4b** and 0.38 g (36%) of **5b**, together with viscous materials (0.1 g).

4b: Mp 178—180 °C (decomp); colorless needles; IR (KBr) 1787, 1719 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.76, 6.96 (each 1H, d, =CH, J=4.2 Hz), 7.2—7.5 (6H, m), 7.5—7.9 (8H, m); MS m/z 439, 437 (M^+). Found: C, 71.35; H, 3.48; N, 9.57%. Calcd for $C_{26}H_{16}N_3O_2Cl$: C, 71.31; H, 3.68; N, 9.60%.

5b: Mp 285—287 °C (decomp); colorless needles; IR (KBr) 1779, 1713 cm^{-1}; MS m/z 548 (M^+). Found: C, 74.19; H, 3.95; N, 10.33%. Calcd for $C_{34}H_{20}N_4O_4$: C, 74.44; H, 3.68; N, 10.22%.

The ^{1}H NMR spectrum did not measured owing to its insolubility in ordinary solvents.

Reaction of the Dichloro-1,2-diazocine (2) with *N*-Methyl-*p*-toluenesulfonamide in the Presence of Silver Oxide. A mixture of **2** (0.65 g, 2.0 mmol), *N*-methyl-*p*-toluenesulfonamide (0.74 g, 4 mmol) and silver oxide (0.9 g, 4.0 mmol) in benzene (50 ml) was refluxed for 6 h. Similar work-up of the reaction mixture and chromatography of the residue on silica gel gave 0.45 g (47%) of 4-chloro-3,8-diphenyl-7-(*N*-methyl-*p*-toluenesulfonamido)-1,2-diazocine (**4c**) (from benzene elution) and 0.21 g (16%) of 4,7-bis(*N*-methyl-*p*-toluenesulfonamido)-3,8-diphenyl-1,2-diazocine (**5c**) (from chloroform elution), together with viscous materials (60 mg).

4c: Mp 168—170 °C (decomp); colorless prisms; IR (KBr) 1605, 1360, 1345 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.09 (3H, s, CH_3), 2.83 (3H, s, N-CH_3), 5.53, 6.51 (each 1H, d, =CH, J=4.2 Hz), 6.4—7.8 (14H, m); MS m/z 477, 475 (M^+). Found: C, 65.31; H, 4.54; N, 8.99%. Calcd for $C_{26}H_{22}N_3O_2Cl$: C, 65.60; H, 4.66; N, 8.83%.

5c: Mp 244—246 °C (decomp); colorless needles; IR (KBr) 1600, 1355 cm^{-1}; MS m/z 624 (M^+). Found: C, 65.28; H, 5.22; N, 9.06%. Calcd for $C_{34}H_{32}N_4O_4S_2$: C, 65.36; H, 5.16; N, 8.97%.

The ^1H NMR spectrum did not measured owing to its insolubility in ordinary solvents.

Reaction of the Dichloro-1,2-diazocine (2) with *o*-Benzosulfimide in the Presence of Silver Oxide. A mixture of **2** (0.65 g, 2.0 mmol), *o*-benzosulfimide (0.73 g, 4 mmol) and silver oxide (0.9 g, 4.0 mmol) in benzene (50 ml) was refluxed for 6 h. Similar work-up of the reaction mixture and the residue was chromatographed on silica gel to give 0.44 g (47%) of 4-chloro-3,8-diphenyl-7-(*o*-benzosulfimido)-1,2-diazocine (**4d**) (from benzene elution) and 0.20 g (16%) of 4,7-bis(*o*-benzosulfimido)-3,8-diphenyl-1,2-diazocine (**5d**) (from chloroform elution), together with viscous materials (40 mg).

4d: Mp 186—187 °C (decomp); colorless prisms; IR (KBr) 1740, 1350, 1335 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.74, 6.98 (each 1H, d, =CH, J=4.2 Hz), 7.2—7.6 (8H, m), 7.6—8.0 (6H, m); MS m/z 475, 473 (M^+). Found: C, 63.28; H, 3.51; N, 8.76%. Calcd for $C_{25}H_{16}N_3O_3Cl$: C, 63.35; H, 3.40; N, 8.87%.

5d: Mp 275—277 °C (decomp); colorless needles; IR (KBr) 1740, 1350 cm^{-1}; MS m/z 620 (M^+). Found: C, 61.77; H, 3.51; N, 8.87%. Calcd for $C_{32}H_{20}N_4O_6S_2$: C, 61.92; H, 3.25; N, 9.03%.

4-Acetoxy-3,8-diphenyl-7-phthalimido-1,2-diazocine (6). A mixture of 1.30 g (3.0 mmol) of the chloro-phthalimido-1,2-diazocine (**4b**) and 2.9 g (9 mmol) of lead acetate in benzene (60 ml) was refluxed for 20 h. The reaction mixture was filtered, and the precipitate was washed with chloroform (50 ml). The combined filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel to give 0.20 g (15%) of the unchanged **4b** (from benzene elution) and 0.65 g (47%) of the acetoxy-phthalimido-1,2-diazocine (**6**) (from chloroform elution).

6: Mp 195—196 °C (decomp); colorless prisms; IR (KBr) 1760, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.93 (3H, s, CH_3), 6.38, 6.91 (each 1H, d, =CH, δ=4.2 Hz), 7.1—7.4 (6H, m), 7.4—7.8 (8H, m); MS m/z 461 (M^+). Found: C, 72.61; H, 3.91; N, 9.02%. Calcd for $C_{28}H_{19}N_3O_4$: C, 72.87; H, 4.15; N, 9.11%.

3,8-Diphenyl-4-phenylthio-7-phthalimido-1,2-diazocine (7). A mixture of 1.30 g (3.0 mmol) of the chloro-phthalimido-1,2-diazocine (**4b**) and benzenethiol (1.0 ml, 9 mmol) in benzene (60 ml) was refluxed for 10 h. After the reaction mixture was washed with a 10% aqueous sodium hydroxide solution, the benzene solution was concentrated in vacuo to leave a residue. The residue was chromatographed on silica gel to give 70 mg (5%) of the unchanged **4b** (from benzene elution) and 0.98 g (65%) of the phenylthio-phthalimido-1,2-diazocine (**7**) (from chloroform elution).

7: Mp 222—223 °C (decomp); colorless prisms; IR (KBr) 1780, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.44, 6.95 (each 1H, d, =CH, J=4.2 Hz), 7.1—7.5 (12H, m), 7.5—7.8 (7H, m); MS m/z 511 (M^+). Found: C, 75.33; H, 4.11; N, 8.29%. Calcd for $C_{32}H_{21}N_3O_2S$: C, 75.12; H, 4.14; N, 8.22%.

Thermolysis of the Mono(succinimido)-1,2-diazocine (4a). A suspension of **4a** (1.0 g, 2.6 mmol) in dry xylene (20 ml) was refluxed for 5 h; the reaction mixture turned to a clear solution after 30 min, and then a precipitate gradually formed. After the reaction mixture had been cooled to room temperature, it was filtered to give 0.41 g (35%) of the bis(succinimido)-1,2-diazocine (**5a**). The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel to give 0.11 g (15%) of 6-chloro-2-phenyl-3-succinimidopyridine (**8a**) and 70 mg (8%) of 6-benzoyl-2-phenyl-3-succinimidopyridine (**9a**) (each from benzene elution), together with 0.15 g of viscous materials (from chloroform and ethyl acetate elutions).

8a: Mp 187—188 °C; yellow prisms; IR (KBr) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.2—2.8 (4H, m, CH_2), 7.40, 7.49 (each 1H, d, PyH, J=8.0 Hz), 7.43 (5H, s); MS m/z 288, 286 (M^+). Found: C, 62.80; H, 3.93; N, 9.86%. Calcd for $C_{15}H_{11}N_2O_2Cl$: C, 62.84; H, 3.87; N, 9.77%.

9a: Mp 140—142 °C; yellow prisms; IR (KBr) 1700, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.3—2.9 (4H, m, CH_2), 7.35—7.7 (8H, m), 7.80, 8.16 (each 1H, d, PyH, J=8.2 Hz), 8.0—8.4 (2H, m); MS m/z 356 (M^+). Found: C, 74.29; H, 4.39; N, 7.54%. Calcd for $C_{22}H_{16}N_2O_3$: C, 74.14; H, 4.53; N, 7.86%.

Thermolysis of the Mono(phthalimido)-1,2-diazocine (4b). A suspension of **4b** (1.0 g, 2.3 mmol) in dry xylene (20 ml) was refluxed for 5 h; during which time the reaction mixture turned to a clear solution. The reaction mixture was concentrated in vacuo, and the residue was chromatographed (silica gel, benzene) to give 40 mg (17%) of benzonitrile, 0.32 g (42%) of 6-chloro-2-phenyl-3-phthaliminopyridine (**8b**) and 0.28 g (30%) of 6-benzoyl-2-phenyl-3-phthaliminopyridine (**9b**). In this case, any bis(phthalimido)-1,2-diazocine (**5b**) did not formed.

8b: Mp 139—140 °C; yellow prisms; IR (KBr) 1780, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.2—7.7 (7H, m), 7.7—7.9 (4H, m); MS m/z 336, 334 (M^+). Found: C, 68.33; H, 3.21; N, 8.10%. Calcd for $C_{19}H_{11}N_2O_2Cl$: C, 68.17; H, 3.31; N, 8.37%.

9b: Mp 173—174 °C; yellow prisms; IR (KBr) 1780, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.2—8.3 (14H, m), 7.87, 8.11 (each 1H, d, PyH, J=8.2 Hz); MS m/z 404 (M^+). Found: C, 77.27; H, 3.45; N, 6.77%. Calcd for $C_{26}H_{16}N_2O_3$: C, 77.21; H, 3.39; N, 6.93%.

Thermolysis of the Mono(*o*-benzosulfimido)-1,2-diazocine (4d). A suspension of **4d** (1.0 g, 2.1 mmol) in dry xylene (20 ml) was refluxed for 5 h; the reaction mixture turned to a clear solution after 30 min, and then a precipitate gradually separated out. After the mixture had been cooled, filtration gave 0.38 g (29%) of the bis(*o*-benzosulfimido)-1,2-diazocine (**5d**). The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel to give trace amounts of benzonitrile, 70 mg (9%) of 3-(*o*-benzosulfimido)-6-chloro-2-phenylpyridine (**8d**), 0.10 g (11%) of 6-benzoyl-3-(*o*-benzosulfimido)-2-phenylpyridine (**9d**), 80 mg (17%) of 3,6-dichloro-2-phenylpyridine (**10**), mp 100—101 °C (lit,[2] mp 100—101 °C), and 30 mg (5%) of 6-benzoyl-3-chloro-2-phenylpyridine (**11**), mp 119—120 °C (lit,[2] mp 119—120 °C) (each from benzene elution), together with 0.2 g of viscous materials (from chloroform and ethyl acetate elutions).

8d: Mp 196—197 °C; yellow prisms; IR (KBr) 1730, 1340, 1305 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.1—7.5 (6H, m), 7.5—8.0 (5H, m); MS m/z 372, 370 (M^+). Found: C, 58.11; H, 3.06; N, 7.77%. Calcd for $C_{18}H_{11}N_2O_3SCl$: C, 58.30; H, 2.99; N, 7.56%.

9d: Mp 103—104 °C; yellow prisms; IR (KBr) 1730, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.12—7.57 (8H, m), 7.57—7.97 (5H, m), 7.97—8.27 (3H, m); MS m/z 440 (M^+). Found: C, 67.99; H, 3.76; N, 6.57%. Calcd for $C_{25}H_{16}N_2O_4S$: C, 68.17; H, 3.66; N, 6.36%.

3-Amino-6-chloro-2-phenylpyridine (12). i) A solution of 0.1 g of the succinimidopyridine (**8a**) in ethanol (30 ml) containing potassium hydroxide (0.5 g) was refluxed for 3 h.

The reaction mixture was concentrated in vacuo, and water (30 ml) was added to the residue which was extracted with chloroform (50 ml×2). The chloroform extract was concentrated in vacuo, and the residue was chromatographed (silica gel, chloroform) to give 30 mg (42%) of the aminopyridine (**12**).

12: Mp 98—99 °C; yellow prisms; IR (KBr) 3450, 3400, 3350, 3300 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.7 (2H, broad, NH_2), 7.04 (2H, s, PyH), 7.36—7.76 (5H, m); MS *m/z* 206, 204 (M^+). Found: C, 64.57; H, 4.51; N, 13.77%. Calcd for $C_{11}H_9N_2Cl$: C, 64.55; H, 4.43; N, 13.69%.

ii) A solution of 0.1 g of the *o*-benzosulfimidopyridine (**8d**) in ethanol (30 ml) containing potassium hydroxide (0.5 g) was refluxed for 3 h. The reaction mixture was concentrated in vacuo, and the residue was triturated with water (30 ml) to turn a solution. The aqueous solution was acidified with hydrochloric acid, and then extracted with chloroform (30 ml×2). The extract was concentrated in vacuo to leave 70 mg (67%) of *o*-[(6-chloro-2-phenyl-3-pyridyl)sulfamoyl]benzoic acid (**13**) (mp 184—186 °C; IR (KBr) 2400—3200, 1705, 1340 cm^{-1}; MS *m/z* 390 (M^+)). The pyridine **13** (70 mg) was heated in concd hydrochloric acid (20 ml) under reflux, and then the reaction mixture was concentrated in vacuo. The obtained residue was triturated with a 10% aqueous potassium hydroxide solution (15 ml), and then extracted with chloroform (30 ml×2). The extract was concentrated in vacuo, and the residue was chromatographed (silica gel, benzene) to give 20 mg (54%) of **12**.

Conversion of the Pyridine (9b) into 6-Benzoyl-3-hydroxy-2-phenylpyridine (15). A solution of **9b** (0.8 g) in ethanol (50 ml) containing potassium hydroxide (1.0 g) was refluxed for 4 h. The reaction mixture was poured into water (200 ml), and then extracted with benzene (100 ml×2). The benzene extract was concentrated in vacuo, and the residue was chromatographed (silica gel, chloroform) to give 0.41 g (78%) of 3-amino-6-benzoyl-2-phenylpyridine (**14**).

14: Mp 172—173 °C; yellow prisms; IR (KBr) 3500, 3400, 3350, 1640, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.33 (2H, broad, NH_2), 7.10, 7.99 (each 1H, d, PyH, *J*=8.2 Hz), 7.33—7.93 (6H, m), 8.03—8.33 (4H, m); MS *m/z* 274 (M^+). Found: C, 78.90; H, 5.11; N, 10.40%. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.15; N, 10.21%.

After diazotization of 0.27 g of the pyridine (**14**) with sodium nitrite in aqueous sufluric acid (concd sufuric acid (4 ml) and water (30 ml)) at 0—5 °C, the reaction mixture was heated at 60 °C for 2 h. The mixture was extracted with chloroform (50 ml×2) and the extract was concentrated in vacuo to leave 0.11 g (41%) of the pyridine (**15**),[2] mp 172—173 °C, which was identical with an authentic sample prepared from hydrolysis of 3-acetoxy-6-benzoyl-2-phenylpyridine.

Thermolysis of the Bis(phthalimido)-1,2-diazocine (5b). The diazocine **5b** (1.0 g) in a test tube was heated at 300—310 °C (bath temp) for 15 min. The pyrolysate was chromatographed on silica gel to give 80 mg (43%) of benzonitrile and 0.16 g (20%) of 3,6-bis(phthalimido)-2-phenylpyridine (**16**) (each from benzene elution), together with 0.5 g of viscous materials (from chloroform and ethyl acetate elution).

16: Mp 303—305 °C; yellow prisms; IR (KBr) 1780, 1720 cm^{-1}; ^1H NMR (DMSO-d_6) δ=7.15—7.35 (5H, m), 7.71, 8.23 (each 1H, d, PyH, *J*=8.2 Hz), 7.8—8.0 (8H, m); MS *m/z* 445 (M^+). Found: C, 72.56; H, 3.54; N, 9.62%. Calcd for $C_{27}H_{15}N_3O_4$: C, 72.80; H, 3.39; N, 9.43%.

Thermolysis of the Acetoxy-phthalimido-1,2-diazocine (6). The diazocine **6** (1.0 g) in test tube was heated at 230—240 °C (bath temp) for 15 min. The pyrolysate was chromatographed on silica gel to give 10 mg of benzonitrile, 0.10 g (11%) of the benzoylpyridine (**9b**) and 80 mg (10%) of 6-acetoxy-2-phenyl-3-phthalimidopyridine (**17**) (each from benzene elution), together with 0.5 g of viscous materials (from chloroform and ethyl acetate elution).

17: Mp 228—230 °C; yellow prisms; IR (KBr) 1780, 1760, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.37 (3H, s), 7.1—7.7 (7H, m), 7.7—8.0 (4H, m); MS *m/z* 358 (M^+). Found: C, 70.64; H, 3.83; N, 7.64%. Calcd for $C_{21}H_{14}N_2O_4$: C, 70.38; H, 3.94; N, 7.82%.

Thermolysis of the Phenylthio-1,2-diazocine (7). The diazocine **7** (0.9 g) in a test tube was heated at 240—260 °C (bath temp) for 15 min. Chromatography (silica gel) of the pyrolysate afforded 30 mg (16%) of benzonitrile, trace amounts of diphenyl disulfide, 0.18 g (25%) of 2-phenyl-6-phenylthio-3-phthalimidopyridine (**18**) and 50 mg (7%) of 2-phenyl-3-phenylthio-6-phthalimidopyridine (**19**) (each from benzene elution), together with 0.4 g of viscous materials (from chloroform and ethyl acetate elution).

18: Mp 193—194 °C; colorless needles; IR (KBr) 1780, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.87 (1H, d, PyH, *J*=8.2 Hz), 7.0—7.8 (15H, m); MS *m/z* 408 (M^+). Found: C, 73.74; H, 3.69; N, 6.62%. Calcd for $C_{25}H_{16}N_2O_2S$: C, 73.51; H, 3.95; N, 6.86%.

19: Mp 174—176 °C; colorless needles; IR (KBr) 1780, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.05—7.65 (10H, m), 7.65—8.0 (6H, m); MS *m/z* 408 (M^+). Found: C, 73.40; H, 3.87; N, 6.66%. Calcd for $C_{25}H_{16}N_2O_2S$: C, 73.51; H, 3.95; N, 6.86%.

Hydrolysis of the Pyridine (18). A solution of **18** (0.15 g) in ethanol (30 ml) containing potassium hydroxide (0.5 g) was refluxed for 3 h. After the reaction mixture was concentrated in vacuo, the residue was triturated with water (50 ml) which was extracted with chloroform (30 ml×2). The extract was concentrated in vacuo, and the residue was chromatographed (silica gel, chloroform) to give 60 mg (60%) of 3-amino-2-phenyl-6-phenylthiopyridine (**20**).

20: Mp 119—120 °C; colorless prisms; IR (KBr) 3460, 3300, 3150, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.80 (2H, broad s, NH_2), 6.88 (2H, s, PyH), 7.1—7.7 (10H, m); MS *m/z* 278 (M^+). Found: C, 73.11; H, 5.31; N, 10.22%. Calcd for $C_{17}H_{14}N_2S$: C, 73.35; H, 5.07; N, 10.06%.

Hydrolysis of the Pyridine (19). A solution of **19** (0.1 g) in ethanol (30 ml) containing potassium hydroxide (0.5 g) was refluxed for 3 h. Similar work-up of the reaction mixture, and chromatography (silica gel, chloroform) of the residue gave 40 mg (57%) of 6-amino-2-phenyl-3-phenylthiopyridine (**21**), mp 177—178 °C (lit,[3] mp 177—178 °C).

References

1) B. M. Trost and R. M. Cory, *J. Am. Chem. Soc.*, **93**, 5573 (1971); B. M. Trost, P. H. Schudder, R. M. Cory, N. J. Turro, V. Ramamurthy, and T. J. Katz, *J. Org. Chem.*, **44**, 1264 (1979).

2) S. Yogi, K. Hokama, and O. Tsuge, *Chem. Lett.*, **1982**, 1579; S. Yogi, K. Hokama, K. Ueno, and O. Tsuge, *Bull. Chem. Soc. Jpn.*, **59**, 1087 (1986).

3) S. Yogi, K. Hokama, and O. Tsuge, *Bull. Chem. Soc. Jpn.*, **60**, 335 (1987).

4) S. Yogi, K. Hokama, and O. Tsuge, *Bull. Chem. Soc. Jpn.*, **60**, 343 (1987).