

# Synthesis of Pyrrolo[2,1-*a*]phthalazines by 1,3-Dipolar Cycloaddition of Phthalazinium *N*-Ylides with Alkenes in the Presence of Tetrakis-Pyridine Cobalt (II) Dichromate

Jian Zhou [a], Yuefei Hu\* [a,b] and Hongwen Hu [a,b]

[a] Department of Chemistry and [b] Coordination Chemistry Institute, Nanjing University, Nanjing 210093, People's Republic of China

Received September 24, 1999

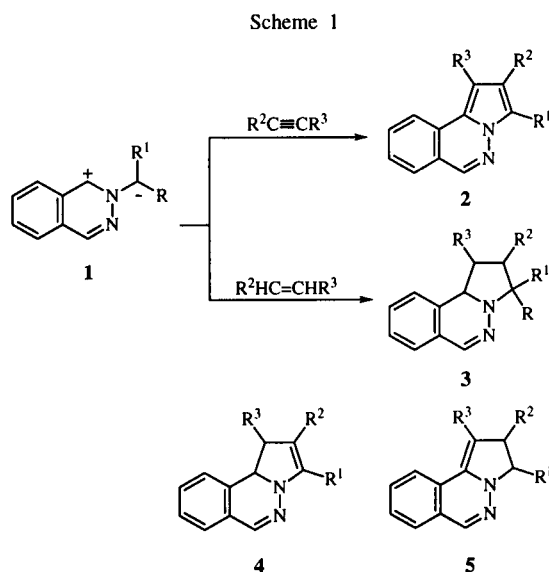
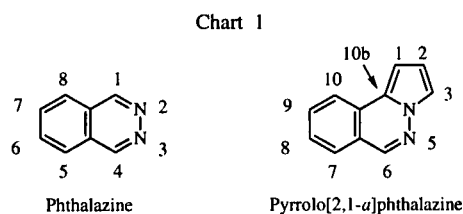
We describe here, for the first time, that 1-cyano-3-benzoyl-1,2,3,10b-tetrahydropyrrolo[2,1-*a*]phthalazine (**8**), prepared by 1,3-dipolar cycloaddition of 2-phenacyl phthalazinium bromide (**6a**) with acrylonitrile (**7a**), can be aromatized by tetrakis-pyridine cobalt (II) dichromate (TPCD) to give 1-cyano-3-benzoylpyrrolo[2,1-*a*]phthalazine (**9a**) in good yield. Furthermore, a general and convenient one-pot procedure for preparation of pyrrolo[2,1-*a*]phthalazines (**9a-p**) was developed by 1,3-dipolar cycloaddition of phthalazinium *N*-ylides (**6a-c**) with alkenes (**7a-g**) in the presence of TPCD.

*J. Heterocyclic Chem.*, **37**, 1165 (2000).

As a result of an increasing interest in their biological activities, derivatives of pyrrolo[2,1-*a*]phthalazine have attracted more attention in recent years [1]. As a part of our studies on the synthesis of *N*-containing heterocyclic compounds for their evaluation in agricultural chemistry, a series of derivatives of pyrrolo[2,1-*a*]phthalazine were designed as target products for synthesis (Chart 1). We wish to report here a facile one-step synthesis of pyrrolo[2,1-*a*]phthalazines by 1,3-dipolar cycloaddition of phthalazinium *N*-ylides with alkenes in the presence of tetrakis-pyridine cobalt (II) dichromate [ $\text{Py}_4\text{Co}(\text{HCrO}_4)_2$ , TPCD]. The procedure was conducted in convenient conditions and gave the products in moderate to good yields.

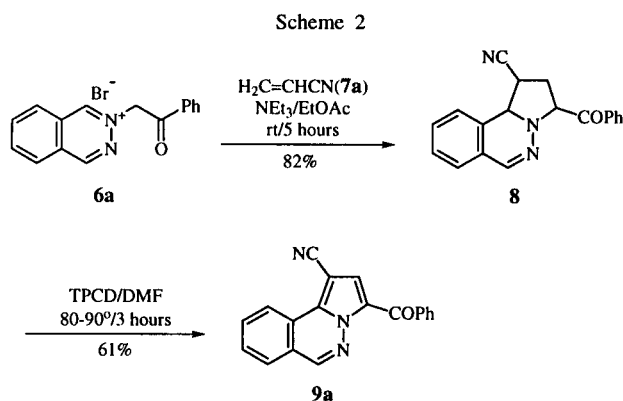
Derivatives of pyrrolo[2,1-*a*]phthalazine could be obtained by multi-step ring closure reactions or by using Reissert salts as precursors [1d,2]. However, the method to build the skeleton of pyrrolo[2,1-*a*]phthalazines by 1,3-dipolar cycloaddition of phthalazinium *N*-ylides had shown more attraction [3,4]. The 1,3-dipolar cycloaddition of phthalazinium *N*-ylides (**1**) with electron-deficient alkynes usually yields pyrrolo[2,1-*a*]phthalazines (**2**), or mixtures with 2,3-dihydropyrrolo[2,1-*a*]phthalazines (**4**) or 1,10b-dihydropyrrolo[2,1-*a*]phthalazines (**5**) [3], depending on the substituents and reaction conditions (Scheme 1). The fact that the dialkyl acetylenedicarboxylates are the only dipolarophiles used in most cases in the literature is likely because the other electron-deficient alkynes are not commercially available and inconvenient to prepare in laboratories. Thus, the range of C1 and C2 functionalized pyrrolo[2,1-*a*]phthalazines that have been prepared by this method is quite limited.

The 1,3-dipolar cycloaddition of phthalazinium *N*-ylides to electron-deficient alkenes, instead of alkynes, normally led to 1,2,3,10b-tetrahydropyrrolo[2,1-*a*]phthalazines (**3**) in good to high yields (Scheme 1) [3c,4]. In some cases, 2,3-dihydropyrrolo[2,1-*a*]phthalazines (**4**) [3c] or 1,10b-dihydropyrrolo[2,1-*a*]phthalazines (**5**) [5] were produced.



Only a very few alkenes with special structures give pyrrolo[2,1-*a*]phthalazines (**2**) directly [3a,6]. Investigation of the literature showed that 2,3-dihydropyrrolo[2,1-*a*]phthalazine (**4**) can be dehydrogenated by MnO<sub>2</sub> to afford pyrrolo[2,1-*a*]phthalazine in high yield [5]. However, no attempt was made for aromatization of 1,2,3,10b-tetrahydropyrrolo[2,1-*a*]phthalazines (**3**) so far, despite its obvious attractiveness for the preparation of pyrrolo[2,1-*a*]phthalazines (**2**).

In our previous works, the versatile oxidant tetrakispyridine cobalt (II) dichromate [Py<sub>4</sub>Co(HCrO<sub>4</sub>)<sub>2</sub>, TPCD] was developed [7] and found to be highly effective for the aromatization of *N*-containing heterocyclic compounds [8]. These results prompted us to try to prepare pyrrolo[2,1-*a*]phthalazines (**2**) by dehydrogenation of 1,2,3,10b-tetrahydropyrrolo[2,1-*a*]phthalazine (**3**). Following the known procedure [3c,4], 1-cyano-3-benzoyl-1,2,3,10b-tetrahydropyrrolo[2,1-*a*]phthalazine (**8**) was prepared in 82% yield by 1,3-dipolar cycloaddition of 2-phenacyl phthalazinium bromide (**6a**) with acrylonitrile (**7a**) in the presence of triethylamine. When compound **8** in DMF was treated with TPCD at 80-90° for 3 hours, 1-cyano-3-benzoylpyrrolo[2,1-*a*]phthalazine (**9a**) was obtained smoothly in 61% as white crystals (Scheme 2).



Upon further exploration, it was found that the sequence of 1,3-dipolar cycloaddition and dehydrogenation (shown in Scheme 2) could be combined into a one-pot reaction. Thus, when a mixture of 2-phenacylphthalazinium bromide (**6a**), acrylonitrile (**7a**), triethylamine and TPCD in DMF was heated at 80-90° for 3 hours, 1-cyano-3-benzoylpyrrolo[2,1-*a*]phthalazine (**9a**) was obtained in 62% yield. By the same procedure, several other phthalazinium salts (**6b-c**) and electron-deficient alkenes (**7b-g**) were examined and the corresponding pyrrolo[2,1-*a*]-

phthalazines (**9b-p**) were obtained in 46-81% yields (Scheme 3 and Table 1). The results showed that the one-pot procedure not only simplified the experimental conditions, but also gave the products in higher overall yields.

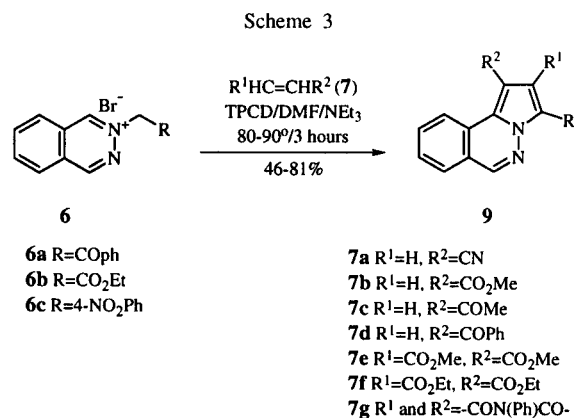


Table 1  
Pyrrolo[2,1-*a*]phthalazine **9a-p**

<b>9</b>	R	R <sup>1</sup>	R <sup>2</sup>	Yields (%)
<b>a</b>	COPh	H	CN	67
<b>b</b>	COPh	H	CO <sub>2</sub> Me	55
<b>c</b>	COPh	H	COMe	50
<b>d</b>	COPh	H	COPh	60
<b>e</b>	COPh	CO <sub>2</sub> Me	CO <sub>2</sub> Me	81
<b>f</b>	COPh	CO <sub>2</sub> Et	CO <sub>2</sub> Et	65
<b>g</b>	COPh	-CON(Ph)CO-		70
<b>h</b>	CO <sub>2</sub> Et	H	CN	61
<b>i</b>	CO <sub>2</sub> Et	H	CO <sub>2</sub> Me	57
<b>j</b>	CO <sub>2</sub> Et	H	COMe	46
<b>k</b>	CO <sub>2</sub> Et	H	COPh	69
<b>l</b>	CO <sub>2</sub> Et	CO <sub>2</sub> Me	CO <sub>2</sub> Me	60
<b>m</b>	CO <sub>2</sub> Et	CO <sub>2</sub> Et	CO <sub>2</sub> Et	66
<b>n</b>	CO <sub>2</sub> Et	-CON(Ph)CO-		54
<b>o</b>	4-NO <sub>2</sub> Ph	H	CO <sub>2</sub> Me	71
<b>p</b>	4-NO <sub>2</sub> Ph	H	COPh	78

In conclusion, we have found that 1,2,3,10b-tetrahydropyrrolo[2,1-*a*]phthalazines can be dehydrogenated easily by TPCD giving pyrrolo[2,1-*a*]phthalazines in a one-pot procedure following 1,3-dipolar cycloaddition of phthalazinium ylides with alkenes. The procedure is a valuable new addition to existing methods for the synthesis of derivatives of pyrrolo[2,1-*a*]phthalazine.

#### EXPERIMENTAL

All melting points were determined on a Yanaco melting point apparatus and are uncorrected. The ir spectra were recorded on a Nicolet FT-IR SDX spectrometer with KBr pellets. The <sup>1</sup>H nmr

spectra were recorded on a Bruker ACF-300 spectrometer with TMS as internal reference. The ms spectra were obtained on a ZAB-HS mass spectrometer with 70 eV. The elemental analyses were performed on a Perkin-Elmer 240C instrument. TPCD was prepared by published procedure [9].

#### General Procedure for Preparation of Phthalazinium Bromides 6a-6c.

A mixture of phthalazine (100 mmoles) and bromide (100 mmoles) in toluene (80 ml) was allowed to stand at room temperature overnight and then stirred at 50-60° for another 5 hours. The solid was filtered and washed with toluene (3 x 5 ml) to give salt 6, which was used directly without further purification.

#### 2-Phenacylphthalazinium Bromide (6a).

This compound was obtained as a gray powder in 91% yield. It had mp 195-197°; ir:  $\nu_{\max}$  3002, 1630, 1497, 1448, 1258, 1033, 815, 604  $\text{cm}^{-1}$ .

#### 2-(Carbomethoxymethyl)phthalazinium Bromide (6b).

This compound was obtained as a yellow powder in 95% yield. It had mp 283-285°; ir:  $\nu_{\max}$  3005, 1745, 1480, 1367, 1222, 1203, 778  $\text{cm}^{-1}$ .

#### 2-(4-Nitrobenzyl)phthalazinium Bromide (6c).

This compound was obtained as a white powder in 98% yield. It had mp 206-208°; ir:  $\nu_{\max}$  3008, 1606, 1515, 1340, 778, 732  $\text{cm}^{-1}$ .

#### General Procedure for Preparation of Pyrrolo[2,1-*a*]phthalazines 9a-9p.

A solution of salt 6 (5.0 mmoles), alkene 7 (15.0 mmoles),  $\text{Et}_3\text{N}$  (7.0 mmoles) and TPCD (5.0 mmoles) in DMF (40 ml) was stirred at 80-90° for 3 hours. Then it was cooled to room temperature and 5% aqueous HCl (100 ml) was added. The precipitate was collected by centrifugation and was dried in air to give crude product 9, which was purified by chromatography [silica gel, 25% EtOAc in petroleum ether (60-90°)].

#### 1-Cyano-3-benzoylpyrrolo[2,1-*a*]phthalazine (9a).

This compound was obtained as white crystals, mp 225-226°; ir:  $\nu_{\max}$  3051, 2221, 1652, 1595, 1469, 766, 723, 695  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  8.90-8.86 (m, 2H), 7.99-7.96 (m, 2H), 7.93 (d, 2H, J = 7.4 Hz), 7.83 (t, 1H, J = 7.6 Hz), 7.64 (t, 1H, J = 7.4 Hz), 7.54 (t, 2H, J = 7.4 Hz), 7.46 (s, 1H); ms: m/z (%) 297 (27), 220 (45), 192 (13), 165 (40), 105 (29), 77 (100).

Anal. Calcd. for  $\text{C}_{19}\text{H}_{11}\text{N}_3\text{O}$ : C, 76.76; H, 3.73; N, 14.13. Found: C, 76.74; H, 3.94; N, 14.27.

#### Methyl 3-Benzoylpyrrolo[2,1-*a*]phthalazine-1-carboxylate (9b).

This compound was obtained as white needles, mp 229-231°; ir:  $\nu_{\max}$  3030, 1708, 1637, 1384, 1244, 1173, 766, 702, 667  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  9.86 (d, 1H, J = 8.2 Hz), 8.97 (s, 1H), 7.97-7.91 (m, 4H), 7.77 (t, 1H, J = 7.5 Hz), 7.72 (s, 1H), 7.62 (t, 1H, J = 7.6 Hz), 7.55 (t, 2H, J = 7.6 Hz), 3.94 (s, 3H); ms: m/z (%) 330 (100), 299 (24), 271 (16), 253 (61), 105 (24), 77 (38).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3$ : C, 72.72; H, 4.27; N, 8.48. Found: C, 72.48; H, 4.52; N, 8.51.

#### 1-Acetyl-3-benzoylpyrrolo[2,1-*a*]phthalazine (9c).

This compound was obtained as white crystals, mp 208-210°; ir:  $\nu_{\max}$  1660, 1630, 1518, 1398, 775, 723, 700  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$

9.86 (d, 1H, J = 8.2 Hz), 8.78 (s, 1H), 7.96-7.90 (m, 4H), 7.78 (t, 1H, J = 7.4 Hz), 7.65-7.62 (m, 2H), 7.53 (t, 2H, J = 7.7 Hz), 2.68 (s, 3H); ms: m/z (%) 314 (69), 299 (100), 237 (11), 77 (11).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2$ : C, 76.42; H, 4.49; N, 8.91. Found: C, 76.42; H, 4.67; N, 8.91.

#### 1,3-Dibenzoylpyrrolo[2,1-*a*]phthalazine (9d).

This compound was obtained as white crystals, mp 200-202°; ir:  $\nu_{\max}$  1635, 1620, 1595, 1510, 875, 765, 720, 702  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  9.19 (d, 1H, J = 8.3 Hz), 8.83 (s, 1H), 7.94-7.92 (m, 5H), 7.85 (t, 1H, J = 7.8 Hz), 7.76 (t, 1H, J = 7.4 Hz), 7.61-7.56 (m, 2H), 7.52-7.46 (m, 4H), 7.35 (s, 1H); ms: m/z (%) 376 (100), 299 (85), 271 (14), 105 (25), 77 (23).

Anal. Calcd. for  $\text{C}_{25}\text{H}_{16}\text{N}_2\text{O}_2$ : C, 79.77; H, 4.28; N, 7.44. Found: C, 79.69; H, 4.20; N, 7.37.

#### Dimethyl 3-Benzoylpyrrolo[2,1-*a*]phthalazine-1,2-dicarboxylate (9e).

This compound was obtained as white needles, mp 171-173°; ir:  $\nu_{\max}$  1721, 1715, 1640, 1225, 1219, 1192, 1162, 770, 700  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  8.78 (d, 1H, J = 8.3 Hz), 8.48 (s, 1H), 7.86-7.79 (m, 4H), 7.67 (t, 1H, J = 8.5 Hz), 7.60 (t, 1H, J = 7.6 Hz), 7.46 (t, 2H, J = 7.6 Hz), 4.01 (s, 3H), 3.57 (s, 3H); ms: m/z (%) 388 (100), 357 (30), 329 (27), 311 (43), 270 (18), 105 (24), 77 (42).

Anal. Calcd. for  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_5$ : C, 68.04; H, 4.15; N, 7.21. Found: C, 67.73; H, 4.20; N, 7.25.

#### Diethyl 3-Benzoylpyrrolo[2,1-*a*]phthalazine-1,2-dicarboxylate (9f).

This compound was obtained as white crystals, mp 124-125°; ir:  $\nu_{\max}$  1730, 1710, 1652, 1600, 1231, 1220, 1189, 760, 704  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  8.81 (d, 1H, J = 8.3 Hz), 8.51 (s, 1H), 7.92 (d, 2H, J = 7.7 Hz), 7.88-7.82 (m, 2H), 7.69 (t, 1H, J = 7.4 Hz), 7.63 (t, 1H, J = 7.7 Hz), 7.45 (t, 2H, J = 7.6 Hz), 4.52 (q, 2H, J = 7.2 Hz), 4.06 (q, 2H, J = 7.2 Hz), 1.45 (t, 3H, J = 7.2 Hz), 1.04 (t, 3H, J = 7.2 Hz); ms: m/z (%) 416 (100), 371 (15), 343 (14), 299 (25), 105 (37), 77 (39).

Anal. Calcd. for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_5$ : C, 69.22; H, 4.84; N, 6.73. Found: C, 69.42; H, 4.87; N, 6.61.

#### 4-Benzoyl-2-phenyl-1*H*-pyrrolo[3':4':3,4]pyrrolo[2,1-*a*]phthalazine-1,3(2*H*)-dione (9g).

This compound was obtained as white needles, mp 283-285°; ir:  $\nu_{\max}$  1757, 1710, 1648, 1500, 748, 690  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  9.08 (d, 1H, J = 8.0 Hz), 8.76 (s, 1H), 8.06 (d, 2H, J = 7.7 Hz), 7.80 (t, 1H, J = 7.7 Hz), 7.96 (d, 1H, J = 7.7 Hz), 7.84 (t, 1H, J = 7.7 Hz), 7.66 (t, 1H, J = 7.7 Hz), 7.51 (t, 2H, J = 7.7 Hz), 7.47-7.35 (m, 5H); ms: m/z (%) 417 (100), 77 (12).

Anal. Calcd. for  $\text{C}_{26}\text{H}_{15}\text{N}_3\text{O}_3$ : C, 74.81; H, 3.62; N, 10.07. Found: C, 74.93; H, 3.76; N, 10.23.

#### Ethyl 1-Cyanopyrrolo[2,1-*a*]phthalazine-3-carboxylate (9h).

This compound was obtained as white needles, mp 199-201°; ir:  $\nu_{\max}$  3005, 2220, 1722, 1241, 1217, 758  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  8.89-8.86 (m, 2H), 8.00-7.97 (m, 2H), 7.83 (t, 1H, J = 7.5 Hz), 7.76 (s, 1H), 4.48 (q, 2H, J = 7.2 Hz), 1.46 (t, 3H, J = 7.2 Hz); ms: m/z (%) 265 (82), 220 (65), 192 (100), 165 (30).

Anal. Calcd. for  $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_2$ : C, 67.92; H, 4.18; N, 15.84. Found: C, 67.66; H, 4.29; N, 15.68.

#### Methyl Ethyl Pyrrolo[2,1-*a*]phthalazine-1,3-dicarboxylate (9i).

This compound was obtained as white crystals, mp 191-193°; ir:  $\nu_{\max}$  3002, 1710, 1690, 1252, 1228, 1212, 1160, 765, 758  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr:  $\delta$  9.82 (d, 1H, J = 8.4 Hz), 8.78 (s, 1H), 8.00 (s, 1H),

7.91-7.88 (m, 2H), 7.75-7.72 (m, 1H), 4.44 (q, 2H,  $J = 7.2$  Hz), 3.97 (s, 3H), 1.43 (t, 3H,  $J = 7.2$  Hz); ms:  $m/z$  (%) 298 (100), 267 (15), 253 (59), 239 (15), 195 (35).

*Anal.* Calcd. for  $C_{16}H_{14}N_2O_4$ : C, 64.42; H, 4.73; N, 9.39. Found: C, 64.62; H, 4.75; N, 9.49.

Ethyl 1-Acetylpyrrolo[2,1-*a*]phthalazine-3-carboxylate (**9j**).

This compound was obtained as white crystals, mp 174-176°; ir:  $\nu_{\max}$  3100, 1710, 1660, 1380, 1230, 1210, 875, 770  $cm^{-1}$ ;  $^1H$  nmr:  $\delta$  9.80 (d, 1H,  $J = 8.6$  Hz), 8.79 (s, 1H), 7.93 (s, 1H), 7.89-7.86 (m, 2H), 7.75-7.72 (m, 1H), 4.45 (q, 2H,  $J = 7.0$  Hz), 2.72 (s, 3H), 1.45 (t, 3H,  $J = 7.0$  Hz); ms:  $m/z$  (%) 282 (100), 267 (96), 239 (30), 237 (26).

*Anal.* Calcd. for  $C_{16}H_{14}N_2O_3$ : C, 68.08; H, 5.00; N, 9.92. Found: C, 68.18; H, 5.00; N, 9.87.

Ethyl 1-Benzoylpyrrolo[2,1-*a*]phthalazine-3-carboxylate (**9k**).

This compound was obtained as white needles, mp 193-195°; ir:  $\nu_{\max}$  1718, 1640, 1231, 1210, 1071, 968, 882  $cm^{-1}$ ;  $^1H$  nmr:  $\delta$  9.20 (d, 1H,  $J = 8.3$  Hz), 8.85 (s, 1H), 7.95-7.91 (m, 3H), 7.83 (t, 1H,  $J = 7.6$  Hz), 7.75-7.72 (m, 1H), 7.64 (t, 2H,  $J = 7.6$  Hz), 7.56-7.53 (m, 2H), 4.42 (q, 2H,  $J = 7.1$  Hz), 1.39 (t, 3H,  $J = 7.1$  Hz); ms:  $m/z$  (%) 344 (100), 299 (24), 272 (22), 267 (31), 239 (12), 195 (20).

*Anal.* Calcd. for  $C_{21}H_{16}N_2O_3$ : C, 73.24; H, 4.68; N, 8.13. Found: C, 73.29; H, 4.67; N, 8.28.

Dimethyl Ethyl Pyrrolo[2,1-*a*]phthalazine-1,2,3-tricarboxylate (**9l**).

This compound was obtained as white crystals, mp 125-126°; ir:  $\nu_{\max}$  3010, 3005, 1731, 1720, 1700, 1498, 1230, 1200, 770  $cm^{-1}$ ;  $^1H$  nmr:  $\delta$  9.50 (d, 1H,  $J = 8.6$  Hz), 8.80 (s, 1H), 7.92-7.89 (m, 2H), 7.78-7.75 (m, 1H), 4.46 (q, 2H,  $J = 7.0$  Hz), 4.00 (s, 3H), 3.97 (s, 3H), 1.43 (t, 3H,  $J = 7.0$  Hz); ms:  $m/z$  (%) 356 (18), 239 (26), 221 (100), 194 (42).

*Anal.* Calcd. for  $C_{18}H_{16}N_2O_6$ : C, 60.67; H, 4.53; N, 7.86. Found: C, 60.80; H, 4.64; N, 7.77.

Triethyl Pyrrolo[2,1-*a*]phthalazine-1,2,3-tricarboxylate (**9m**).

This compound was obtained as white needles, mp 106-108°; ir:  $\nu_{\max}$  3010, 3004, 1735, 1720, 1708, 1228, 1205, 1162, 1108, 762  $cm^{-1}$ ;  $^1H$  nmr:  $\delta$  9.49 (d, 1H,  $J = 8.3$  Hz), 8.76 (s, 1H), 7.88-7.85 (m, 2H), 7.74-7.71 (m, 1H), 4.46-4.39 (m, 6H), 1.44-1.38 (m, 9H); ms:  $m/z$  (%) 384 (5), 312 (29), 265 (100), 239 (27).

*Anal.* Calcd. for  $C_{20}H_{20}N_2O_6$ : C, 62.49; H, 5.24; N, 7.29. Found: C, 62.45; H, 5.35; N, 7.37.

4-Ethoxycarbonyl-2-phenyl-1*H*-pyrrolo[3'4':3,4]pyrrolo[2,1-*a*]phthalazine-1,3(2*H*)-dione (**9n**).

This compound was obtained as white needles, mp 301°; ir:  $\nu_{\max}$  1738, 1712, 1500, 1272, 1240, 770, 748  $cm^{-1}$ ;  $^1H$  nmr:  $\delta$  9.09 (d, 1H,  $J = 8.0$  Hz), 8.87 (s, 1H), 8.01-7.97 (m, 2H), 7.86-7.84 (m, 1H), 7.54-7.42 (m, 5H), 4.55 (q, 2H,  $J = 7.0$  Hz), 1.51 (t, 3H,  $J = 7.0$  Hz); ms:  $m/z$  (%) 385 (100), 340 (18), 313 (40), 312 (16).

*Anal.* Calcd. for  $C_{22}H_{15}N_3O_4$ : C, 68.57; H, 3.92; N, 10.90. Found: C, 68.62; H, 3.89; N, 10.93.

Methyl 3-(4-Nitrophenyl)pyrrolo[2,1-*a*]phthalazine-1-carboxylate (**9o**).

This compound was obtained as yellow crystals, mp 181-183°; ir:  $\nu_{\max}$  1645, 1588, 1511, 1340, 761, 742, 690  $cm^{-1}$ ;  $^1H$  nmr:  $\delta$

8.43 (d, 1H,  $J = 7.8$  Hz), 8.20-8.17 (m, 3H), 7.86-7.78 (m, 3H), 7.72 (d, 1H,  $J = 7.7$  Hz), 7.62-7.60 (m, 2H), 5.49 (s, 3H); ms:  $m/z$  (%) 347 (2), 132 (100).

*Anal.* Calcd. for  $C_{19}H_{13}N_3O_4$ : C, 65.70; H, 3.77; N, 12.10. Found: C, 65.80; H, 3.64; N, 12.03.

1-Benzoyl-3-(4-nitrophenyl)pyrrolo[2,1-*a*]phthalazine (**9p**).

This compound was obtained as yellow crystals, mp 276-278°; ir:  $\nu_{\max}$  1642, 1602, 1583, 1513, 1340, 760, 740, 688  $cm^{-1}$ ;  $^1H$  nmr:  $\delta$  9.24 (d, 1H,  $J = 8.1$  Hz), 8.70 (s, 1H), 8.32 (d, 2H,  $J = 8.1$  Hz), 8.16 (d, 2H,  $J = 8.1$  Hz), 7.97 (d, 2H,  $J = 6.8$  Hz), 7.89 (d, 1H,  $J = 7.4$  Hz), 7.90-7.82 (m, 2H), 7.69 (t, 1H,  $J = 7.0$  Hz), 7.63 (d, 1H,  $J = 6.8$  Hz), 7.55 (d, 2H,  $J = 6.8$  Hz); ms:  $m/z$  (%) 393 (100), 363 (30), 316 (63), 281 (52).

*Anal.* Calcd. for  $C_{24}H_{15}N_3O_3$ : C, 73.27; H, 3.84; N, 10.68. Found: C, 73.36; H, 3.85; N, 10.72.

Acknowledgment.

We are grateful to Natural Science Foundation of China for financial support.

#### REFERENCES AND NOTES

- [1a] Eur. Pat. Appl. EP 319,330 (1987); *Chem. Abstr.*, **111**, 232846u (1989); [b] M. Caprosu, E. Stefanescu, M. Ungureanu and M. Perrovanu, *Rev. Roum. Chim.*, **36**, 657 (1991); *Chem. Abstr.*, **116**, 235554m (1992); [c] Jpn. Kokai. Tokyo, Koho JP 05 65,215 (1993); *Chem. Abstr.*, **119**, 34097c (1993); [d] A. W. Bridge, M. B. Hursthouse, C. W. Lehmann, D. J. Lythgoe and C. G. Newton. *J. Chem. Soc., Perkin Trans I*, 1839 (1993).
- [2a] B. C. Uff and R. S. Budhram, *Synthesis*, 206 (1978); [b] D. Bhattacharjee and F. D. Popp, *J. Heterocyclic Chem.*, **17**, 1035 (1980); [c] K. T. Potts, K. G. Bordeaux, W. R. Kuehnling and R. L. Salsbury, *J. Org. Chem.*, **50**, 1677 (1985); [d] B. C. Uff, G. Ghaem-Maghani, R. S. Budhram, C. L. Wilson and J. O. Apatu, *J. Heterocyclic Chem.*, **26**, 571 (1989).
- [3a] K. Matsumoto, T. Uchida, Y. Ikemi, T. Tanaka, M. Asahi, T. Kato and H. Konishi, *Bull. Chem. Soc. Jpn.*, **60**, 3645 (1987); [b] M. Caprosu, M. Ungureanu, G. Grosu and M. Perrovanu, *Rev. Med.-Chir.*, **96**, 69 (1992); *Chem. Abstr.*, **119**, 113215t (1993); [c] R. N. Butler, D. M. Farrell and C. S. Pyne, *J. Chem. Res. (S)*, 418 (1996).
- [4a] M. Caprosu, M. Petrovanu, I. Druta, I. Zugravescu, *Bull. Soc. Chim. Fr.*, 1834 (1971); *Chem. Abstr.*, **75**, 49007v (1971); [b] S. Dima, I. Mangalagiu, M. Caprosu, I. Zugravescu, I. Humelnicu and M. Petrovanu, *J. Serb. Chem. Soc.*, **62**, 105 (1997); *Chem. Abstr.*, **126**, 263743x (1997).
- [5] A. F. Khlebnikov, E. I. Kostik and R. R. Kostikov, *Synthesis*, 568 (1993).
- [6a] Y. Tominaga, Y. Ichihara and A. Hosomi, *Heterocycles*, **27**, 2345 (1988); [b] C. H. Weidner, F. M. Michaels, D. J. Beltman, C. J. Montgomery, D. H. Wadsworth, B. T. Briggs and M. L. Picone, *J. Org. Chem.*, **56**, 5594 (1991).
- [7] Y. Hu, X. Wei and H. Hu, in *Encyclopedia of Reagents for Organic Synthesis*, Vol. 7, L. A. Paquette ed, John Wiley & Sons, New York, 1995, p 4780.
- [8a] J. Zhou, Y. Hu and H. Hu, *Synthesis*, 136 (1999); [b] J. Zhou, Y. Hu and H. Hu, *J. Chem. Res. (S)*, 166 (1999); [c] B. Wang, X. Zhang, J. Li, X. Jiang, Y. Hu and H. Hu, *J. Chem. Soc., Perkin Trans. I*, 1571 (1999).
- [9] Y. Hu and H. Hu, *Synth. Commun.*, **22**, 1491 (1992). TPCD also can be purchased directly from Aldrich Chemical Co., Inc. under the name of tetrakis(pyridine) cobalt (II) bischromate.