Synthesis of 1-Aryl-1*H*-pyrazolecarbonitriles and Related Derivatives

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The synthesis of 1-aryl-5-cyano-1*H*-pyrazole-4-carboxylic acid, ethyl esters **1** is described. Subsequent chemistry led to relatively simple and unique pyrazole derivatives. Most important of these are 1-aryl-5-(aminocarbonyl)-1*H*-pyrazole-4-carboxylic acids **2**, which are chemical hybridizing agents in wheat and barley. The regioselective hydrolysis of 1-(3-chlorophenyl)-1*H*-pyrazole-4,5-dicarboxylic acid, dimethyl ester (**7b**) and subsequent chemistry is also described.

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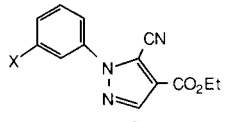
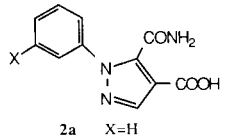
We recently reported [1] the synthesis of 1-aryl-5-chloro-1*H*-pyrazole-4-carboxylic acid, ethyl esters by nonaqueous diazotization of the corresponding amino esters with nitrosyl chloride. Carboxamides derived from these chloro esters were herbicides [2]. Nucleophilic displacement by cyanide ion produced 1-aryl-5-cyano-1*H*-pyrazole-4-carboxylate esters, and the corresponding carboxamides were also herbicides [3]. We now wish to describe the synthesis and subsequent chemistry of these cyano esters.

Treatment of 5-chloro-1-phenyl-1*H*-pyrazole-4-carboxylic acid, ethyl ester [1] with 2 equivalents of sodium cyanide in dimethylformamide at 100-130° for 2.5 hours gave the corresponding cyano ester **1a** in 80% yield. Similarly prepared was the 3-chlorophenyl derivative **1b** (85%). Basic hydrolysis of **1a** and **1b** converted the cyano function to the carboxamide and the ester to the carboxylic acid to yield **2a** (88%) and **2b** (87%), respectively. Compound **2b** was found to produce male sterility in wheat and barley plants, and represents a new class of chemical hybridizing agents in cereal crops [4].



1a X=H
1b X=Cl



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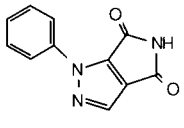
2b X=Cl



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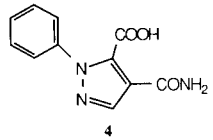

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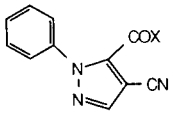
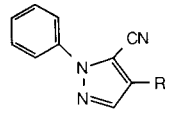
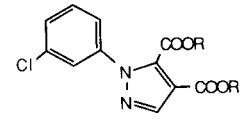


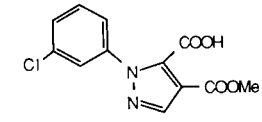
5a X=OH
5b X=OMe
5c X=NHMe



6a R=COOH
6b R=H
6c R=CON3
6d R=NHCOOt-Bu
6e R=NH2



7a R=H
7b R=Me



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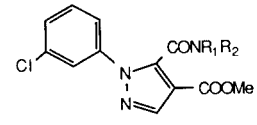
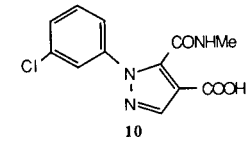


9a $R_1=R_2=H$
9b $R_1=H$; $R_2=CH_3$



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Reaction with 1,1'-carbonyldiimidazole converted **2a** to the imide **3** (67%). With stronger dehydrating agents, such as thionyl chloride-dimethylformamide, **2a** was simply dehydrated to the cyano acid **6a**, which was more readily prepared by mild basic hydrolysis of **1a** as will be described later. Treatment of **3** with hydroxide ion led to reaction at the more activated carbonyl with ring opening to give compound **4** (69%), which is isomeric with **2a** with functionality at C-4 and C-5 reversed. When **4** was allowed to react with thionyl chloride-dimethylformamide in refluxing toluene, two transformations occurred. The carboxylic acid was converted to its acid chloride and the carboxamide was dehydrated to the corresponding nitrile. Aqueous workup yielded the cyano acid **5a** (80%). Treatment of the crude acid chloride with methanol or methylamine gave the cyano ester **5b** (88%) and the cyano carboxamide **5c** (70%), respectively.

Mild basic hydrolysis of **1a** produced the cyano acid **6a** (86%), which was decarboxylated in quinoline-copper at 180° to yield 1-phenyl-1*H*-pyrazole-5-carbonitrile (**6b**, 80%). Compound **6a** was readily converted to the corresponding carbonyl azide **6c** (86%). Curtius rearrangement in the presence of *t*-butyl alcohol gave the carbamate derivative **6d** (84%). Hydrolysis of **6d** with hydrobromic acid in acetic acid yielded the amino nitrile **6e** (59%).

Compound **2b** was hydrolysed in refluxing 48% hydrobromic acid in order to obtain the corresponding dicarboxylic acid **7a** (89%). Treatment of **7a** with methanolic hydrogen chloride gave the dimethyl ester **7b** (87%) [5]. Reaction of **7b** with hydroxide ion under relatively mild conditions occurred at the more activated carbonyl (as in the case of the imide **3**) and yielded the half acid ester **8** (67%). Treatment of **8** with 1,1′-carbonyldiimidazole in dimethylformamide, followed by the addition of ammonium hydroxide or aqueous methylamine, produced the half amide esters **9a** (61%) and **9b** (63%), respectively. Compound **9a** was identical with the product obtained by reaction of **2b** with methanolic hydrogen chloride, thus verifying the assigned structure of the half acid ester **8**. Basic hydrolysis of **9b** gave the half amide acid **10** (60%).

In summary, we have described the preparation of 1-aryl-5-cyano-1*H*-pyrazole-4-carboxylate esters **1a-b**, which led to the synthesis of unique pyrazole derivatives. Most of the reactions described have been examined with numerous substituted aryls at the 1-position. For the sake of brevity, these were not included in this paper. Many examples of compounds related to **1** [3], **2** [4], **6a** [3], and **9a** [4] have been described in a recently issued U. S. Patent and a European Patent application. We have also discussed the selective hydrolysis of 1-(3-chlorophenyl)-1*H*-pyrazole-4,5-dicarboxylic acid, dimethyl ester (**7b**) and the subsequent chemistry of the half acid ester **8**. Jones and Whitehead [5] described a similar acid catalyzed selective hydrolysis of 1*H*-pyrazole-4,5-dicarboxylic acid, diethyl ester.

EXPERIMENTAL [6]

5-Cyano-1-phenyl-1*H*-pyrazole-4-carboxylic Acid, Ethyl Ester (**1a**).

A solution containing 31.0 g (0.124 mole) of 5-chloro-1-phenyl-1*H*-pyrazole-4-carboxylic acid, ethyl ester [1] and 12.0 g (0.245 mole) of finely ground sodium cyanide in 100 ml of dimethylformamide was stirred and heated at 130° for 0.5 hour and at 110° for 2 hours. The mixture was poured into ice water. The crude solid was collected and crystallized from ethanol-water to yield 23.9 g (80%) of product, mp 74-75°; ^{1}H nmr (deuteriochloroform): δ 8.19 (s, 1H), 7.5-7.8 (m, 5H), 4.45 (q, 2H), 1.45 (t, 3H).

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.89; H, 4.52; N, 17.62.

1-(3-Chlorophenyl)-5-cyano-1*H*-pyrazole-4-carboxylic Acid, Ethyl Ester (**1b**).

A solution containing 8.5 g (0.030 mole) of 5-chloro-1-(3-chlorophenyl)-1*H*-pyrazole-4-carboxylic acid, ethyl ester [1] and 2.9 g (0.059 mole) of finely ground sodium cyanide in 75 ml of dimethylformamide was stirred and heated at 100° for 5 hours. The mixture was poured into ice water. The solid was collected and crystallized from ethanol to yield 7.0 g (85%) of product, mp 93-95°; ^{1}H nmr: (deuteriochloroform): δ 8.22 (s, 1H), 7.5-7.8 (m, 4H), 4.46 (q, 2H), 1.44 (t, 3H).

Anal. Calcd. for $C_{13}H_{10}ClN_3O_2$: C, 56.64; H, 3.66; N, 15.24. Found: C, 56.77; H, 3.78; N, 15.15.

5-(Aminocarbonyl)-1-phenyl-1*H*-pyrazole-4-carboxylic Acid (**2a**).

A solution of 15.0 g (0.062 mole) of **1a** and 7.0 g (0.125 mole) of potassium hydroxide in 150 ml of ethanol and 50 ml of water was stirred and refluxed for 1.25 hours. The mixture was poured into ice water and acidified with hydrochloric acid. The product slowly crystallized and was collected to yield 12.6 g (88%) of **2a**, mp 233-235°; ^{1}H nmr (DMSO-d_6): δ 8.38 (s, 1NH), 8.04 (s, 1H), 7.97 (s, 1NH), 7.4-7.6 (m, 5H).

Anal. Calcd. for $C_{11}H_9N_3O_3$: C, 57.14; H, 3.92; N, 18.17. Found: C, 56.89; H, 3.67; N, 17.94.

5-(Aminocarbonyl)-1-(3-chlorophenyl)-1*H*-pyrazole-4-carboxylic Acid (**2b**).

A solution containing 7.0 g (0.025 mole) of **1b** and 2.8 g (0.050 mole) of potassium hydroxide in 150 ml of ethanol was stirred and refluxed for 2 hours. The mixture was poured into ice water and acidified with hydrochloric acid. The product slowly crystallized and was collected to yield 5.8 g (87%) of **2b**, mp 218-220°; ^{1}H nmr (DMSO-d_6): δ 8.44 (s, 1NH), 8.08 (s, 1H), 8.06 (s, 1NH), 7.5-7.65 (m, 4H); ms: m/e 265 (M^+).

Anal. Calcd. for $C_{11}H_8ClN_3O_3$: C, 49.73; H, 3.04; N, 15.82. Found: C, 49.90; H, 2.92; N, 15.87.

1-Phenylpyrrolo[3,4-*c*]pyrazole-4,6(1*H*,5*H*)-dione (**3**)

1,1′-Carbonyldiimidazole (9.7 g, 0.060 mole) was added portionwise to a stirred solution of 12.4 g (0.054 mole) of **2a** in 60 ml of dimethylformamide. The mixture was stirred at ambient temperature for 15 minutes and then heated on the steam bath for 2 hours. The solution was poured into ice water, and the solid was collected and crystallized from acetic acid to yield 7.65 g (67%) of product, mp 207-209°; ir (potassium bromide): 1770, 1730 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 8.12 (s, 2H), 8.10 (s, 1H), 7.61 (t, 2H), 7.47 (t, 1H).

Anal. Calcd. for $C_{11}H_7N_3O_2$: C, 61.97; H, 3.31; N, 19.71. Found: C, 62.18; H, 3.50; N, 19.43.

4-(Aminocarbonyl)-1-phenyl-1*H*-pyrazole-5-carboxylic Acid (**4**).

A solution containing 8.6 g (0.040 mole) of **3** and 3.0 g (0.054 mole) of potassium hydroxide in 100 ml of ethanol was stirred and refluxed for 20 minutes. The mixture was poured into ice water and acidified with hydrochloric acid. The solid was collected and crystallized from acetic acid to yield 6.45 g (69%) of product, mp 228° (gas evolution, solidification and remelting at 238°); ^{1}H nmr (DMSO-d_6): δ 8.42 (s, 1H), 7.4-7.55 (m, 5H).

Anal. Calcd. for $C_{11}H_9N_3O_3$: C, 57.14; H, 3.92; N, 18.17. Found: C, 57.20; H, 3.98; N, 18.06.

4-Cyano-1-phenyl-1*H*-pyrazole-5-carboxylic Acid (**5a**).

A suspension of 1.75 g (7.6 mmoles) of **4** in 30 ml of toluene, 10 ml of thionyl chloride and 0.5 ml of dimethylformamide was stirred and refluxed for 1.5 hours. The solvent and excess thionyl chloride were removed *in vacuo*. Toluene (30 ml) was added and removed *in vacuo*. The crude solid acid chloride was dissolved in 25 ml of acetone and 5 ml of water, and the mixture was heated on the steam bath for 10 minutes. The solution was poured into ice water. The solid was collected and crystallized from toluene to yield 1.3 g (80%) of product, mp 154-155° (gas evolution); ir (potassium bromide): 2240, 1735 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 8.05 (s, 1H), 7.35-7.55 (m, 5H).

Anal. Calcd. for $C_{11}H_7N_3O_2$: C, 61.97; H, 3.31; N, 19.71. Found: C, 61.90; H, 3.36; N, 19.60.

4-Cyano-1-phenyl-1*H*-pyrazole-5-carboxylic Acid, Methyl Ester (**5b**).

The crude acid chloride was prepared as in the synthesis of **5a** starting with 2.2 g (9.5 mmoles) of **4**. The solid was dissolved in 30 ml of methanol, and the mixture was stirred and refluxed for 10 minutes. The hot solution was filtered and the product crystallized to yield 1.9 g (88%) of **5b**, mp 138-139°; ir (potassium bromide): 2230, 1730 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 8.01 (s, 1H), 7.35-7.55 (m, 5H), 3.92 (s, 3H).

Anal. Calcd. for $C_{12}H_9N_3O_2$: C, 63.43; H, 3.99; N, 18.49. Found: C, 63.44; H, 4.20; N, 18.48.

4-Cyano-*N*-methyl-1-phenyl-1*H*-pyrazole-5-carboxamide (**5c**).

The crude acid chloride was prepared as in the synthesis of **5a** utilizing 2.2 g (9.5 mmoles) of **4**. The solid was dissolved in 25 ml of toluene and methylamine was bubbled in for several minutes. The solid was col-

lected and crystallized from ethanol-water to yield 1.5 g (70%) of product, mp 178-180°; ir (potassium bromide): 2230, 1650 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.97 (s, 1H), 7.4-7.5 (m, 5H), 3.00 (d, 3H).

Anal. Calcd. for $C_{12}H_{10}N_4O$: C, 63.71; H, 4.46; N, 24.76. Found: C, 63.42; H, 4.23; N, 24.62.

5-Cyano-1-phenyl-1*H*-pyrazole-4-carboxylic Acid (**6a**).

A solution containing 7.3 g (0.030 mole) of **1a** and 4.0 g (0.071 mole) of potassium hydroxide in 120 ml of ethanol was stirred, heated just to reflux and immediately poured into 200 ml of water. The solution was acidified with hydrochloric acid. The solid was collected and crystallized from toluene to yield 5.5 g (86%) of product, mp 205-206°; ^1H nmr (deuteriochloroform): δ 8.26 (s, 1H), 7.5-7.8 (m, 5H).

Anal. Calcd. for $C_{11}H_7N_3O_2$: C, 61.97; H, 3.31; N, 19.71. Found: C, 61.95; H, 3.08; N, 19.67.

1-Phenyl-1*H*-pyrazole-5-carbonitrile (**6b**).

A solution containing 20.0 g (0.094 mole) of **6a** and 2.0 g of natural copper (fine 44-F) in 80 ml of quinoline was stirred and heated. Decarboxylation commenced at 180°, and the solution was heated at 180-190° for 1 hour. The mixture was poured into ice water and acidified with concentrated sulfuric acid. Following two extractions with diethyl ether the combined organic extract was washed with dilute hydrochloric acid, 2*N* sodium hydroxide and saturated brine solution. The solvent was removed, and the product was distilled to yield 12.7 g (80%) of **6b**, bp 95-100°/0.5-0.75 mm; ir (neat): 2220 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.70-7.75 (m, 2H), 7.68 (d, 1H), 7.4-7.55 (m, 3H), 7.00 (d, 1H).

Anal. Calcd. for $C_{10}H_7N_3$: C, 70.99; H, 4.17; N, 24.84. Found: C, 70.69; H, 4.30; N, 24.58.

5-Cyano-1-phenyl-1*H*-pyrazole-4-carbonyl Azide (**6c**).

A suspension of 2.5 g (11.7 mmoles) of **6a** in 50 ml of toluene and 10 ml of thionyl chloride was stirred and refluxed for 3 hours. The solvent and excess thionyl chloride were removed *in vacuo*. Toluene (50 ml) was added and removed *in vacuo*. The crude acid chloride was dissolved in 25 ml of acetone, and the solution was cooled in an ice bath. Sodium azide (1.0 g, 15.4 mmoles) in 5 ml of water was added dropwise. The solution was warmed to ambient temperature during 1 hour. The mixture was poured into ice water. The solid was collected and crystallized from methanol to yield 2.4 g (86%) of product, mp 128-129° (gas evolution); ir (potassium bromide): 2220, 2140, 1680 cm^{-1}; ^1H nmr (deuteriochloroform): δ 8.18 (s, 1H), 7.5-7.85 (m, 5H).

Anal. Calcd. for $C_{11}H_6N_6O$: C, 55.46; H, 2.54; N, 35.28. Found: C, 55.26; H, 2.47; N, 35.08.

(5-Cyano-1-phenyl-1*H*-pyrazol-4-yl)carbamic Acid, 1,1-Dimethylethyl Ester (**6d**).

A suspension of 2.0 g (8.4 mmoles) of **6c** in 20 ml of toluene was stirred and refluxed for 30 minutes. The reaction was cooled to ambient temperature, and *t*-butyl alcohol (10 ml) was added. The solution was refluxed for 2 hours. Removal of the solvent *in vacuo* and crystallization from ethanol yielded 2.0 g (84%) of product, mp 156-158°; ^1H nmr (deuteriochloroform): δ 8.21 (broad s, 1H), 7.4-7.7 (m, 5H), 1.55 (s, 9H).

Anal. Calcd. for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71. Found: C, 63.13; H, 5.74; N, 19.64.

4-Amino-1-phenyl-1*H*-pyrazole-5-carbonitrile (**6e**).

To a suspension of 2.6 g (9.2 mmoles) of **6d** in 15 ml of acetic acid was added dropwise 10 ml of 30-32% hydrobromic acid in acetic acid. The product crystallized and was collected. It was recrystallized by dissolving it in 200 ml of hot water. As the solution cooled enough ethanol was added to prevent oiling out. The crystals were collected to yield 1.0 g (59%) of product, mp 90-91°; ir (potassium bromide): 2200 cm^{-1}; ^1H nmr (DMSO-d_6): δ 7.38 (s, 1H), 7.3-7.6 (m, 5H).

Anal. Calcd. for $C_{10}H_8N_4$: C, 65.21; H, 4.38; N, 30.42. Found: C, 65.02; H, 4.16; N, 30.21.

1-(3-Chlorophenyl)-1*H*-pyrazole-4,5-dicarboxylic Acid (**7a**).

A suspension of 25.0 g (0.094 mole) of **2b** in 200 ml of 48% hydrobromic acid was stirred and refluxed for 20 minutes. The solution cleared during the heating, and the product crystallized during reflux. The mixture was cooled and the product was collected and washed with cold water to yield 22.4 g (89%) of **7a**, mp 196-197° (gas evolution); ^1H nmr (DMSO-d_6): δ 8.11 (s, 1H), 7.4-7.7 (m, 4H).

Anal. Calcd. for $C_{11}H_7ClN_2O_4$: C, 49.55; H, 2.65; N, 10.51. Found: C, 49.38; H, 2.45; N, 10.59.

1-(3-Chlorophenyl)-1*H*-pyrazole-4,5-dicarboxylic Acid, Dimethyl Ester (**7b**).

Hydrogen chloride was bubbled into 400 ml of cold methanol for 5 minutes. Compound **7a** (47.8 g, 0.179 mole) was added and the mixture was stirred and refluxed for 23 hours. The hot solution was filtered and allowed to crystallize to yield 45.7 g (87%) of product, mp 111-112°; ^1H nmr (deuteriochloroform): δ 8.02 (s, 1H), 7.3-7.55 (m, 4H), 3.88 (s, 3H), 3.85 (s, 3H).

Anal. Calcd. for $C_{13}H_{11}ClN_2O_4$: C, 52.98; H, 3.76; N, 9.51. Found: C, 53.22; H, 3.61; N, 9.64.

1-(3-Chlorophenyl)-1*H*-pyrazole-4,5-dicarboxylic Acid, 4-Methyl Ester (**8**).

To a refluxing solution containing 5.9 g (0.020 mole) of **7b** in 100 ml of methanol was added a solution of 1.0 g (0.025 mole) of sodium hydroxide in 10 ml of water. The mixture was refluxed for 5 minutes and poured into 200 ml of water. It was acidified with hydrochloric acid and allowed to crystallize. The product was collected and recrystallized from methanol-water to yield 3.75 g (67%) of product, mp 141-142°; ^1H nmr (deuteriochloroform): δ 8.22 (s, 1H), 7.2-7.6 (m, 4H), 4.10 (s, 3H).

Anal. Calcd. for $C_{12}H_9ClN_2O_4$: C, 51.35; H, 3.23; N, 9.98. Found: C, 51.56; H, 3.00; N, 10.00.

5-(Aminocarbonyl)-1-(3-chlorophenyl)-1*H*-pyrazole-4-carboxylic Acid, Methyl Ester (**9a**).

Method A.

To a solution containing 1.4 g (5.0 mmoles) of **8** in 10 ml of dimethylformamide was added portionwise 1.0 g (6.2 mmoles) of 1,1'-carbonyldiimidazole. The mixture was stirred for 15 minutes, and concentrated ammonium hydroxide (3 ml) was added dropwise. The mixture was stirred at ambient temperature for 1 hour and poured into ice water. The solid was collected and crystallized from toluene to yield 0.85 g (61%) of product, mp 193-194°; ir (potassium bromide): 1720, 1680 cm^{-1}; ^1H nmr (DMSO-d_6): δ 8.40 (s, 1H), 8.14 (s, 2H), 7.5-7.7 (m, 4H), 3.79 (s, 3H).

Anal. Calcd. for $C_{12}H_{10}ClN_3O_3$: C, 51.53; H, 3.60; N, 15.02. Found: C, 51.48; H, 3.38; N, 14.87.

Method B.

Into a suspension of 2.2 g (8.3 mmoles) of **2b** in 40 ml of methanol was bubbled hydrogen chloride for 1 minute. The mixture was stirred and refluxed for 2 hours. The solution was poured into ice water and basified with 2*N* sodium hydroxide. The solid was collected and crystallized from toluene to yield 1.7 g (73%) of product, mp 191-192°. This derivative gave no mixed melting point depression with the product prepared by Method A, and their ir and nmr spectra were identical.

1-(3-Chlorophenyl)-5-[(methylamino)carbonyl]-1*H*-pyrazole-4-carboxylic Acid, Methyl Ester (**9b**).

To a solution containing 3.6 g (12.8 mmoles) of **8** in 15 ml of dimethylformamide was added portionwise 2.3 g (14.2 mmoles) of 1,1'-carbonyldiimidazole. The mixture was stirred at ambient temperature for 1 hour. Aqueous methylamine (40%, 3 ml) was added and the mixture was stirred for an additional hour. The product crystallized and was collected to yield 2.35 g (63%) of product, mp 165-166°; ^1H nmr (deuteriochloroform): δ 8.11 (s, 1H), 7.25-7.5 (m, 4H), 3.93 (s, 3H), 2.89 (d, 3H).

Anal. Calcd. for $C_{13}H_{12}ClN_3O_3$: C, 53.16; H, 4.12; N, 14.31. Found: C, 53.11; H, 4.33; N, 14.05.

1-(3-Chlorophenyl)-5-[(methylamino)carbonyl]-1*H*-pyrazole-4-carboxylic Acid (**10**).

A solution of 0.6 g (15.0 mmoles) of sodium hydroxide in 5 ml of water was added to a suspension of 1.5 g (5.1 mmoles) of **9b** in 15 ml of methanol. The mixture was brought just to reflux and immediately poured into 50 ml of water. The solution was acidified with hydrochloric acid and allowed to crystallize to yield 1.1 g of product, mp 197-202°. Recrystallization from methanol-water gave 0.85 g (60%) of product, mp 202-203°; ^{1}H nmr (DMSO-d_6): δ 8.09 (s, 1H), 7.4-7.65 (m, 4H), 2.71 (d, 3H).

Anal. Calcd. for $C_{12}H_{10}ClN_3O_3$: C, 51.53; H, 3.60; N, 15.02. Found: C, 51.74; H, 3.39; N, 15.14.

REFERENCES AND NOTES

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[3] J. R. Beck, U. S. Patent 4,589,905 (1986); see also *Chem. Abstr.*, **103**, 141948x (1985).

[4] J. R. Beck and C. W. Price, Eur. Pat. Appl. EP177,242 (1986); *Chem. Abstr.*, **105**, 148199d (1986).

[5] A more convenient synthesis of 1-aryl-1*H*-pyrazole-4,5-dicarboxylic acids and esters has been reported: R. G. Jones and C. W. Whitehead, *J. Org. Chem.*, **20**, 1342 (1955).

[6] Melting points were determined on a Mel-Temp apparatus and are uncorrected.