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Received November 7, 2001

Reaction of chloropyridazin-3-one **1**, **5** and **10** with catechol in the presence of potassium carbonate gave the corresponding [1,4]benzodioxino[2,3-*c* and/or 2,3-d]pyridazinones **2**, **7**, **8** and **11**.

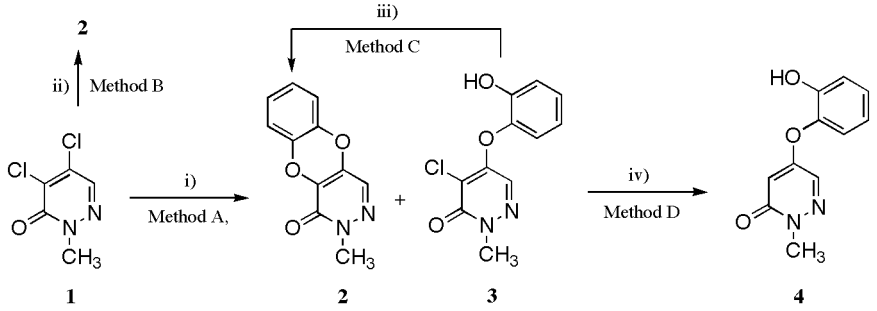
J. Heterocyclic Chem., **39**, 685 (2002).

In connection with our research program for the synthesis of novel aryl heteroaryl cyclic ether containing diazines, we needed to synthesize some [1,4]benzodioxinopyridazinone derivatives. However, there appear to be only few related references [1-3]. Ames *et al.* [1] synthesized 3-chloro[1,4]benzodioxino[2,3-*c*]pyridazine and 1-chloro[1,4]benzodioxino[2,3-*d*]pyridazine from catechol and 3, 4, 5 (or 3, 4, 6)-trichloropyridazine in the presence of potassium carbonate or sodium hydride. Chupp *et al*. [2] also synthesised similar derivatives by the thermal fusion without a base. And Lee *et al.* [3] synthesized the corresponding [1,4]benzodioxino[2,3-*c*]pyridazine by Diels-Alder reaction between 2-vinyl-1,4-benzodioxin and dibenzyl diazodicarboxylate. However, to the best of our knowledge, the synthesis of [1,4]benzodioxinopyridazinone has not been reported. Therefore, we attempted to synthesize the corresponding [1,4]benzodioxino[2,3-*c*, or 2,3-*d*]pyridazinones from 4,5-dichloro-, 4,5,6-trichloro- and 4,5-dichloro-6-nitropyridazin-3-ones under basic condition according to Ames's method [1].

Reaction of **1** (1 equivalent) with catechol (1 equivalent) and one equivalent of potassium carbonate in acetonitrile at reflux temperature gave **2** (43%), **3** (16%) (Method A). But, compound **1** (1 equivalent) was reacted with catechol (1 equivalent) in the presence of excess potassium carbonate (2.5 equivalents) to afford only **2** in 90% yield (Method B). Cyclization of **3**, in the presence of potassium carbonate (1 equivalent) in acetonitrile, also afforded compound **2** in 93% yield (Method C). According to our observation by monitoring tlc, compound **3** was formed in the first step and then cyclized to **2** in the second step. The structures of **2** and **3** were established by ir, nmr and elemental analysis. In the infrared spectrum of **2**, the absorption band of one amide carbonyl was observed; whereas, the infrared spectrum of **3** showed the absorption bands of one amide carbonyl and one OH group. The proton magnetic resonance spectra of **2** and **3** showed proton signals for CH_3 (δ 3.76 for **2**; δ 3.77 for **3**) as singlet, phenyl (δ 6.90 for **2**; δ 7.08 for **3**) as multiplet and C6-H for pyridazin-3-one (δ 7.52 for **2**; δ 7.37 for **3**) as singlet, and also showed the proton signal of OH for **3** at δ 9.60 as singlet. The ^{13}C nmr spectra for **2** and **3** also showed signals for the carbons of methyl, carbonyl and phenyl groups involving the other carbons of pyridazinone.

In order to establish the position of the phenoxy group for **3**, compound **3** was dechlorinated with $Pd/C/H_2$ in methanol to yield **4** in 81% yield. The position of the phenoxy group for **4** was established by the coupling constant between the

Scheme 1

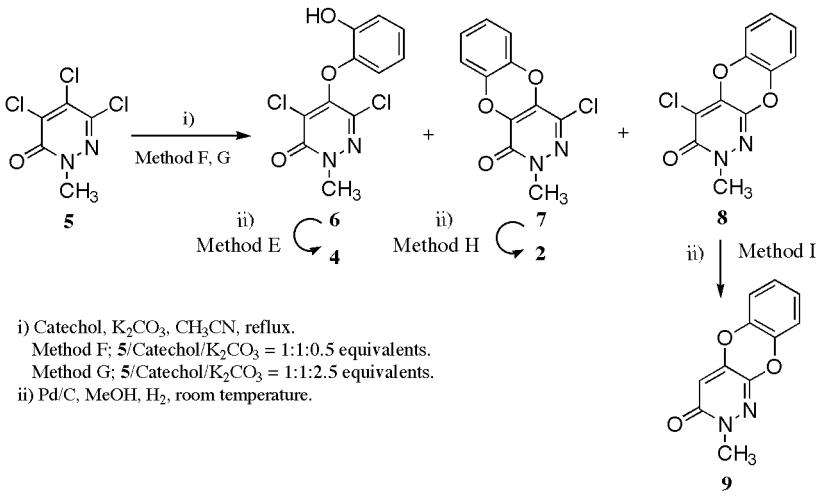


i) Catechol, K_2CO_3,CH_3CN, reflux; Method A: **1**/Catechol/K_2CO_3 = 1:1:1 equivalent.
ii) Catechol, K_2CO_3,CH_3CN, reflux; Method B: **1**/Catechol/K_2CO_3 = 1:1:2.5 equivalents.
iii) K_2CO_3, CH_3CN; Method C. iv) Pd/C, MeOH, H_2, room temperature; Method D.

C4-H and C6-H. According to Katz, *et al.* [4] and Kweon, *et al.* [5], the coupling constant between the C4-H and C6-H for 5-substituted-pyridazin-3-ones is smaller than that between C5-H and C6-H for the 4-substituted isomer ($J_{4,6}$ = about 2Hz, $J_{5,6}$ = about 5Hz). The coupling constant between the C4-H and the C6-H for **4** was 2.8 Hz.

In the infrared spectrum of **13**, we detected the absorption band of NH_2. The pmr spectrum of **13** also showed the proton signals of NH_2 at δ 5.85 involving methyl and phenyl groups. It is easy to establish the position of the phenoxy group for **14** by comparing the chemical shift values of C4-H with that of other 5-substituted derivatives

Scheme 2

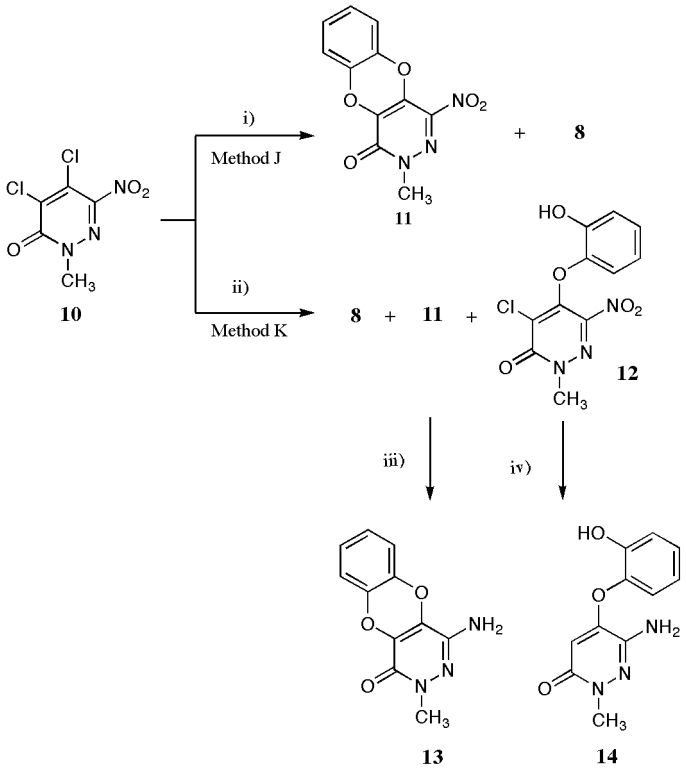


i) Catechol, K_2CO_3, CH_3CN, reflux.
Method F; **5**/Catechol/K_2CO_3 = 1:1:0.5 equivalents.
Method G; **5**/Catechol/K_2CO_3 = 1:1:2.5 equivalents.
ii) Pd/C, MeOH, H_2, room temperature.

Treatment of **5** (1 equivalent) with catechol (1 equivalent) in the presence of potassium carbonate (0.5 equivalent) in acetonitrile gave **6** (50%), **7** (14%) and **8** (10%), whereas reaction of **5** (1 equivalent) with catechol (1 equivalent) in the presence of excess potassium carbonate (2.5 equivalents) in acetonitrile afforded **7** (54%) and **8** (38%). In order to confirm the structures of **6** and **2**, dechlorination of compound **6** or **7** with Pd/C/H_2 in methanol yielded **4** (91%) or **2** (95%) (Method E or H). Compound **8** was also dechlorinated with Pd/C/H_2 in methanol to give **9** in 88% yield (method I). According to our observation during this reaction by monitoring tlc, compound **6** was also formed in the first step and then cyclized to **7** or **8** in the second step. The infrared spectrum of **6** showed the absorption bands of OH and amide carbonyl. The structures of **6** - **9** were established by ir, nmr, elemental analyses and further reactions.

Reaction of **10** (1 equivalent) with catechol (1 equivalent) in the presence of potassium carbonate (0.5 equivalents) in acetonitrile afforded **8** (29%), **11** (28%) and **12** (19%) (Method K), whereas compound **10** (1 equivalent) was reacted with catechol (1 equivalent) in the presence of excess potassium carbonate (2.2 equivalents) to give **8** (29%) and **11** (22%) (Method J). In order to establish the structure, compound **11** was reduced with NH_4Cl/Fe/CH_2Cl_2/H_2O to give **13** in 90% yield. In order to establish the structure, dechlorination of **12** with Pd/C/H_2 in methanol gave 6-amino-5-(2-hydroxyphenoxy)-2-methylpyridazin-3-one (**14**). The structures of **8** and **11** - **14** were established by ir, nmr and elemental analyses.

Scheme 3



i) **10** /Catechol/K_2CO_3 = 1:1:2.2 equivalents, CH_3CN, room temperature (Method J).
ii) **10** /Catechol/K_2CO_3 = 1:1:0.5 equivalents, CH_3CN, room temperature (Method K).
iii) NH_4Cl, Fe, CH_2Cl_2, H_2O, reflux. iv) Pd/C, MeOH, H_2, room temperature.

such as **4**. The chemical shift value of C4-H is smaller than that of C6-H for 5-substituted derivatives. According to our observation by monitoring tlc, the reaction of **10** with catechol in the presence of potassium carbonate occurred in two steps; **12** was formed in the first step and then cyclized to **8** or **11** in the second step.

Finally, the carbon at the 5-position on the pyridazine ring is the most reactive site for phenoxide in 4,5-dichloro-, 4,5,6-trichloro- and 4,5-dichloro-6-nitro-2-alkylpyridazin-3-ones. And multichloropyridazin-3-ones are useful materials for the synthesis of [1,4]benzodioxino[2,3-*c* or 2,3-*d*]pyridazinones.

Further work including the chemical transformation, complexation and biological activity of novel compounds is under way in our laboratory.

EXPERIMENTAL

Melting points were determined with a Thomas-Hoover capillary apparatus and are uncorrected. Magnetic resonance spectra were obtained on a Brüker FTNMR-DRX 500 spectrometer with chemical shift values reported in δ units (part per million) relative to an internal standard (tetramethylsilane). Infrared spectral data were obtained on a Hitachi 270-50 spectrophotometer. Elemental analyses were performed with a Perkin Elmer 240C. Open-bed chromatography was carried out on silica gel 60 (70-230 mesh, Merck) using gravity flow. The column was packed as slurries with the elution solvent. Compounds **1** [6], **5** [6] and **10** [7] were prepared according to the reported methods.

Reaction of 4,5-Dichloropyridazin-3-one (1) with Catechol.

Method A.

A mixture of **1** (10 g, 56 mmoles), catechol (6.2 g, 56 mmoles), potassium carbonate (7.7 g, 56 mmoles) and acetonitrile (150 mL) was refluxed for 23 hours. After cooling to room temperature, the reaction mixture was filtered and washed with chloroform (10 mL x 5) and then methanol (10 mL). The combined filtrate was evaporated under reduced pressure. The residue was applied to the top of an open-bed silica gel column (3 x 20 cm). The column was eluted with chloroform. Fractions containing **2** (R_f = 0.4, chloroform/diethyl ether = 9.5:0.5, v/v) were combined and evaporated under reduced pressure. The resulting residue was recrystallized from diethyl ether to give **2** in 43% (5.6 g) yield. mp 201-202°; ir (potassium bromide): 3100, 3050, 2970, 2905, 1680, 1650, 1610, 1500, 1395, 1320, 1290, 1145, 970, 760 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.76 (s, 3H), 6.90 (m, 4H), 7.52 ppm (s, 1H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 40.1, 116.8, 117.7, 125.5, 125.9, 129.5, 135.2, 140.0, 140.5, 141.2, 155.4 ppm.

Anal. Calcd. for $C_{11}H_8N_2O_3$: C, 61.11; H, 3.73: N, 12.96. Found: C, 61.34; H, 3.61: N, 13.07.

Fractions containing **3** (R_f = 0.1, chloroform/diethyl ether = 9.5:0.5, v/v) were combined and evaporated under reduced pressure. The resulting residue was recrystallized from chloroform/diethyl ether to give **3** in 16% (2.3 g) yield. mp 206-207°; ir (potassium bromide): 3400-3000, 1638, 1515, 1460, 1390, 1290, 1240, 750 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.77 (s, 3H), 7.08 (m, 4H), 7.37 (s, 1H), 9.60 ppm (s, OH, deuterium oxide exchangeable); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 40.5, 116.8, 117.8, 120.1, 121.8, 127.4, 128.5, 140.5, 148.8, 154.3, 158.8 ppm.

Anal. Calcd. for $C_{11}H_9N_2O_3Cl$: C, 52.29; H, 3.59: N, 11.09. Found: C, 52.37; H, 3.52: N, 11.07.

Method B.

A mixture of **1** (0.5 g, 2.79 mmoles), catechol (0.3 g, 2.79 mmoles), potassium carbonate (1 g, 6.98 mmoles) and acetonitrile (40 mL) was refluxed for 6.5 hours. After cooling to room temperature, the reaction mixture was filtered and washed with methylenechloride (10 mL x 5). The combined filtrate was evaporated under reduced pressure. The residue was triturated in water (100 mL). The mixture was filtered, and the residue was then washed with diethyl ether (20 mL) and dried in air to afforded **2** in 90% (0.54 g) yield.

Cyclization of **3** to **2**.

Method C.

A mixture of **3** (0.5 g, 1.98 mmoles), potassium carbonate (0.27 g, 1.98 mmoles) and acetonitrile (20 mL) was refluxed for 24 hours. After cooling to room temperature, the reaction mixture was filtered and washed with chloroform (10 mL). The combined filtrate was evaporated under reduced pressure. The resulting residue was applied to the top of an open-bed silica gel column (5 x 2.5 cm). The column was eluted with chloroform. Fractions containing **2** were combined and evaporated under reduced pressure to afford **2** in 93% (0.4 g) yield. This product was identical with **2** that were prepared by the Method A.

2-Methyl-5-(2-hydroxyphenoxy)pyridazin-3-one (**4**).

Method D.

A mixture of Pd/C (0.3 g), **3** (0.5 g, 1.98 mmoles) and methanol (20 mL) was stirred for 16 hours under a hydrogen atmosphere (using a toy balloon) at room temperature. After removal of the catalyst by filtration using Celite 545, the residue was washed with methanol (10 mL). The solution was evaporated under reduced pressure. The resulting residue was applied to the top of an open-bed silica gel column (3 x 8 cm). The column was eluted with chloroform. Fractions containing the product were combined and evaporated under reduced pressure. The residue was triturated in diethyl ether. The mixture was filtered and dried in air to give **4** in 81% (0.35 g) yield. mp 191-192°; ir (potassium bromide): 3400-3000, 2970, 2750, 1645, 1595, 1520, 1470, 1405, 1350, 1290, 1240, 1195, 1030, 850, 780, 740 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.60 (s, 3H), 5.62 (d, 1H, J = 2.8), 7.10 (m, 4H), 7.95 (d, 1H, J = 2.8), 9.92 ppm (s, OH, deuterium oxide exchangeable); ^{13}C (dimethyl sulfoxide-d_6): δ 38.8, 104.9, 117.6, 119.9, 122.3, 127.5, 131.4, 139.2 148.7, 159.1, 160.7 ppm.

Anal. Calcd. for $C_{11}H_{10}N_2O_3$: C, 60.55; H, 4.62: N, 12.84. Found: C, 60.67; H, 4.70: N, 12.89.

Method E.

A mixture of Pd/C (0.2 g), **6** (0.15 g, 0.52 mmoles) and methanol (15 mL) was allowed to stirr for 22 hours under a hydrogen atmosphere (using a toy balloon) at room temperature. After removal of the catalyst by filtration using Celite 545, the residue was washed with methanol (10 mL). The solution was

evaporated under reduced pressure. The resulting residue was applied to the top of an open-bed silica gel column (3 x 8 cm). The column was eluted with chloroform. Fractions containing the product were combined and evaporated under reduced pressure. The residue was triturated in diethyl ether. The mixture was filtered and dried in air to give **4** in 91% (0.1 g) yield. This product was identical with **4** that were prepared by the Method D.

Reaction of 4,5,6-Trichloro-2-methylpyridazin-3-one (**5**) with Catechol.

Method F.

A mixture of **5** (0.7 g, 3.28 mmoles), catechol (0.36 g, 3.28 mmoles), potassium carbonate (0.23 g, 1.64 mmoles) and acetonitrile (15 mL) was stirred for 40 minutes at room temperature. The mixture was filtered and washed with methylene chloride (10 mL x 3). The combined filtrate was evaporated under reduced pressure. The residue was applied to the top of an open-bed silica gel column (2.5 x 12 cm). The column was eluted with methylene chloride. Fractions containing **6** (R_f = 0.2, methylene chloride) were combined and the solvent was evaporated off under reduced pressure. The resulting residue was recrystallized from diethyl ether to give **6** in 50% (0.3 g) yield. mp 154-155°; ir (potassium bromide): 3400-3000, 2960, 2875, 1658, 1590, 1505, 1300, 1275, 1170, 1010, 990, 770 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.60 (s, 3H), 6.83 (m, 4H), 9.63 ppm (s, OH, deuterium oxide exchangeable); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 39.0, 116.6, 117.7, 118.9, 123.9, 124.5, 135.2, 143.2, 146.7, 149.5, 154.3 ppm.

Anal. Calcd. for $C_{11}H_8N_2O_3Cl_2$: C, 46.02; H, 2.81: N, 9.76. Found: C, 46.10; H, 2.91: N, 9.81.

Fractions containing **7** or **8** were also combined and the solvent evaporated off under reduced pressure. The resulting residue was recrystallized from diethyl ether to give **7** (14%) or **8** (10 %) yield, respectively. Compound **7**: mp 225-226°; ir (potassium bromide): 3100, 3050, 1690, 1640, 1600, 1500, 1390, 1310, 1265, 1245, 1145, 1060, 990, 920, 770 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.74 (s, 3H), 6.95 ppm (m, 4H); ^{13}C nmr (deuteriochloroform): δ 40.7, 117.5, 118.0, 126.3, 126.7, 130.2, 136.6, 137.9, 140.6, 141.1, 155.0 ppm.

Anal. Calcd. for $C_{11}H_7N_2O_3Cl$: C, 52.71; H, 2.82: N, 11.18. Found: C, 52.81; H, 2.96: N, 2.88. These found values do not match calculated. If these are in error please replace with actual values at the galley proof stage. Please be advised that editorial policy requires a value within ± 0.4 of calculated for carbon and hydrogen.

Compound **8**: mp 219-220°; ir (potassium bromide): 3100, 2970, 1680, 1659, 1630, 1510, 1445, 1300, 1070, 920, 770 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.70 (s, 3H), 7.10 ppm (m, 4H) ; ^{13}C nmr (deuteriochloroform): δ 35.1, 112.1, 112.3, 112.7, 120.2, 121.0, 133.5, 134.5, 135.5, 137.4, 153.0 ppm.

Anal. Calcd. for $C_{11}H_7N_2O_3Cl$: C, 52.71; H, 2.82: N, 11.18. Found: C, 52.78; H, 2.90: N, 11.23.

Method G.

A mixture of **5** (1.0 g, 4.68 mmoles), catechol (0.52 g, 4.68 mmoles), potassium carbonate (1.62 g, 11.71 mmoles) and acetonitrile (50 mL) was stirred for 40 minutes at room temperature. The reaction mixture was then filtered and washed with chloroform (30 mL). The combined filtrate was evaporated under reduced pressure. The residue was applied to the top of an open-bed silica gel column (2.5 x 30 cm). The column was eluted with *n*-hexane/ethyl acetate (5:1, v/v). Fractions containing **8** (R_f = 0. 4, *n*-hexane/ethyl acetate = 1:1, v/v) were combined and evaporated under reduced pressure. The resulting residue was recrystallized from diethyl ether to give **8** in 38% (0.45 g) yield.

Fractions containing **7** (R_f = 0.35, *n*-hexane/ethyl acetate = 1:1, v/v) were combined and evaporated under reduced pressure. The resulting residue was recrystallized from diethyl ether to give **7** in 54% (0.63 g) yield.

Dechlorination of a Mixture of **7** or **8**.

Method H.

A mixture of Pd/C (0.2 g), **7** (0.3 g, 1.20 mmoles) and methanol (20 mL) was stirred for 3 hours under a hydrogen atmosphere (using a toy balloon) at room temperature. After removal of the catalyst by filtration using Celite 545, the residue was washed with methanol (10 mL). The solution was evaporated under reduced pressure to give **2** in 95% (0.25 g) yield. This product was identical with **2** that were prepared by the Method A.

Method I.

A mixture of Pd/C (0.2 g), **8** (0.2 g, 0.80 mmoles) and methanol (20 mL) was stirred for 2.6 hours under a hydrogen atmosphere (using a toy balloon) at room temperature. After removal of the catalyst by filtration using Celite 545, the residue was washed with methanol (10 mL). The solution was evaporated under reduced pressure to give **9** in 88% (0.15 g) yield. mp 212-213°; ir (potassium bromide): 3150, 3050, 2950, 1680, 1640, 1510, 1480, 1295, 780, 760 cm^{-1}; ^1H nmr (deuteriochloroform + dimethyl sulfoxide-d_6): δ 3.50 (s, 3H), 6.30 (s, 1H), 6.95 ppm (m, 4H); ^{13}C nmr (deuteriochloroform + dimethyl sulfoxide-d_6): δ 38.8, 109.9, 116.7, 117.0. 124.8, 125.3, 138.5, 139.6, 141.0, 146.3, 161.1 ppm.

Anal. Calcd. for $C_{11}H_8N_2O_3$: C, 61.11; H, 3.73: N, 12.96. Found: C, 61.22; H, 3.81: N, 13.01.

Reaction of 4,5,-Dichloro-6-nitropyridazin-3-one (**10**) with Catechol.

Method J.

A mixture of **10** (1.0 g, 4.46 mmoles), catechol (0.5 g, 4.46 mmoles), potassium carbonate (1.36 g, 9.81 mmoles) and acetonitrile (40 mL) was stirred for 21 hours at room temperature. After filtering the mixture, the filtrate was evaporated under reduced pressure. The residue was applied to the top of an open-bed silica gel column (2.5 x 15 cm). The column was eluted with methylene chloride/*n*-hexane (1:1, v/v). Fractions containing **11** (R_f = 0. 4, methylene chloride) were combined and the solvent evaporated off under reduced pressure. The resulting residue was recrystallized from *n*-hexane to give **11** in 22% (0.25 g) yield. mp 261-262°; ir (potassium bromide): 3125, 3050, 2905, 1695, 1640, 1605, 1560, 1535, 1505, 1390, 1360, 1290, 1250, 1160, 1070, 1010, 875, 810 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.71 (s, 3H), 7.10 ppm (m, 4H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 40.3, 117.1, 117.2, 126.3, 126.6, 134.8, 136.3, 138.7, 139.3, 139.9, 154.1 ppm.

Anal. Calcd. for $C_{11}H_7N_3O_5$: C, 50.58; H, 2.70; N, 16.09. Found: C, 50.61; H, 2.81: N, 16.12.

Fractions containing **8** (R_f = 0.35, methylene chloride) were combined and evaporated under reduced pressure. The resulting residue was recrystallized from diethyl ether to give **8** in 29% (0.32 g).

Method K.

A mixture of **10** (1.0 g, 4.46 mmoles), catechol (0.5 g, 4.46 mmoles), potassium carbonate (0.3 g, 2.23 mmoles) and acetonitrile (40 mL) was stirred for 3.6 hours at room temperature. After filtering the mixture, the filtrate was evaporated under reduced pressure. The residue was applied to the top of an open-bed silica gel column (2.5 x 15 cm). The column was eluted with methylene chloride/*n*-hexane (1:1, v/v). Fractions containing **11** (R_f = 0. 4, methylene chloride) were combined and evaporated under reduced pressure. The resulting residue was recrystallized from *n*-hexane to give **11** in 28% (0.32 g) yield.

Fractions containing **8** (R_f = 0.35, methylene chloride) were combined and evaporated under reduced pressure. The resulting residue was recrystallized from diethyl ether to give **8** in 29% (0.32 g) yield.

Fractions containing **12** (R_f = 0.22, methylene chloride) were combined and evaporated under reduced pressure. The resulting residue was recrystallized from ethyl acetate/*n*-hexane (1:2, v/v) to give **12** in 19 % (0.25 g) yield. mp 131-133°; ir (potassium bromide): 3550, 3500-3100 (broad doublet), 3050, 1650, 1580, 1490, 1465, 1350, 1270, 1230, 1170, 1090, 1050, 760, 750 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.67 (s, 3H), 6.94 (m, 4H), 9.74 ppm (s, OH, deuterium oxide exchangeable); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 38.9, 115.6, 116.6, 117.8, 119.2, 124.8, 143.0, 145.0, 146.7, 150.0, 154.7 ppm.

Anal. Calcd. for $C_{11}H_8N_3O_5Cl$: C, 44.39; H, 2.71: N, 14.12. Found: C, 44.42; H, 2.83: N, 14.23.

4-Amino-2-methyl[1,4]benzodioxino[2,3-*d*]pyridazin-1-one (**13**).

A mixture of **11** (0.3 g, 1.15 mmoles), iron powder (0.5 g), ammonium chloride (1.2 g), water (20 mL) and methylene chloride (20 mL) was refluxed for 2 hours. After cooling at room temperature, the mixture was applied to the top of an open-bed silica gel column (2.5 x 10 cm). The column was eluted with methylene chloride. Fractions containing the product were combined and evaporated under reduced pressure to give **13** in 90% (0.24 g) yield. mp 260-261°; ir (potassium bromide) 3500, 3290, 3200, 2940, 2920, 1690, 1620, 1550, 1510, 1270, 1190, 1125, 980, 760 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.42 (s, 3H), 5.85 (s, 2H, deuterium oxide exchangeable), 7.09 ppm (m, 4H) ; ^{13}C nmr (dimethyl sulfoxide-d_6): δ 39.0, 117.7, 118.0, 126.5, 126.8, 132.8, 134.7, 141.0, 141.6, 142.1, 153.3 ppm.

Anal. Calcd. for $C_{11}H_9N_3O_3$: C, 57.14; H, 3.92; N, 18.17. Found: C, 57.23; H, 4.02: N, 18.24.

4-Amino-2-methyl-5-(2-hydroxyphenoxy)pyridazin-1-one (**14**).

A mixture of Pd/C (0.2 g), **12** (0.3 g, 1.01 mmoles) and methanol (20 mL) was stirred for 14 hours under a hydrogen atmosphere (using a toy balloon) at room temperature. After removal of the catalyst by filtration using Celite 545, the residue was washed with methanol (10 mL). The solution was evaporated under reduced pressure. The residue was applied to the top of an open-bed silica gel column (2.5 x 8 cm). The column was eluted with ethyl acetate. Fractions containing the product were combined and evaporated under reduced pressure to give **14** in 43% (0.1 g) yield. mp 213-214°; ir (potassium bromide) 3450, 3350, 3230, 3060, 2950, 1660, 1630, 1580, 1500, 1465, 1330, 1265, 1205, 760 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.47 (s, 3H), 5.53 (s, NH_2, deuterium oxide exchangeable), 5.81 (s, 1H), 7.01 (m, 4H), 9.80 ppm (s, OH, deuterium oxide exchangeable); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 38.3, 101.8, 117.6, 119.9, 122.4, 126.9, 140.0, 148.3, 148.8, 153.3, 154.0 ppm.

Anal. Calcd for $C_{11}H_{11}N_3O_3$: C, 56.65; H, 4.75; N, 18.02. Found: C, 56.70; H, 4.82: N, 18.14.

Acknowledgments.

This work was supported by the Brain Korea 21 project.

REFERENCES AND NOTES

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