

## ARYLATION OF 1,3-DIMETHYLLUMAZINES BY ARENEDIAZONIUM SALTS

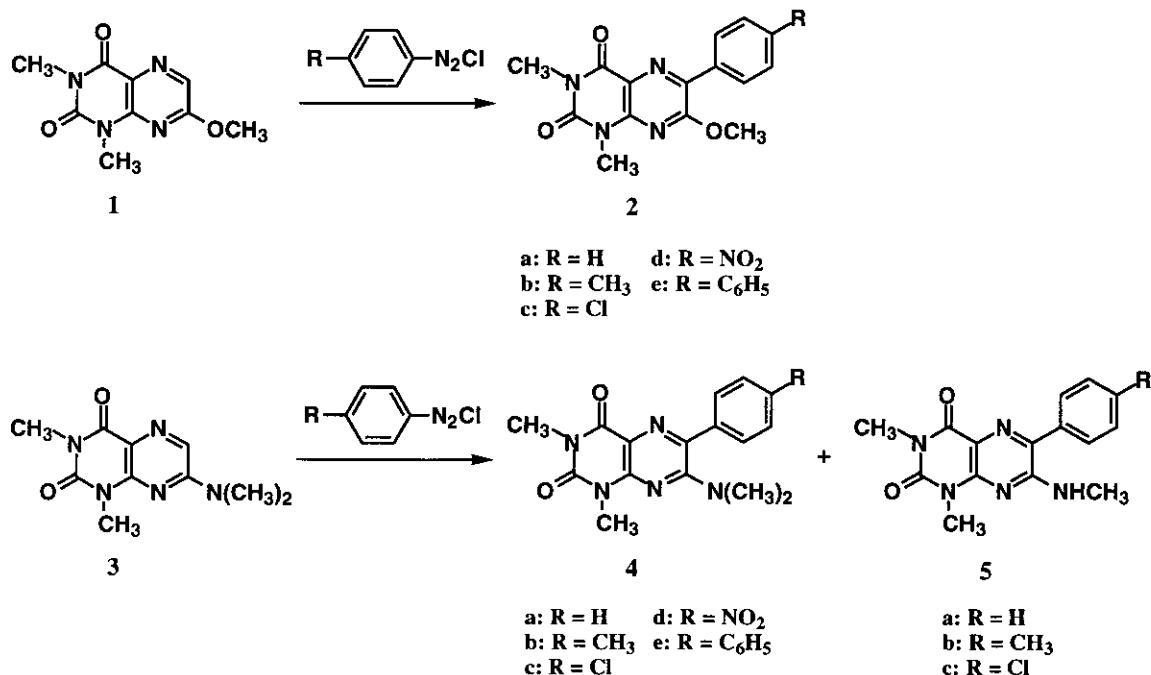
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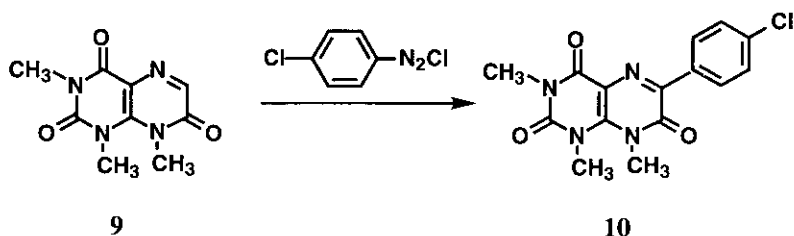
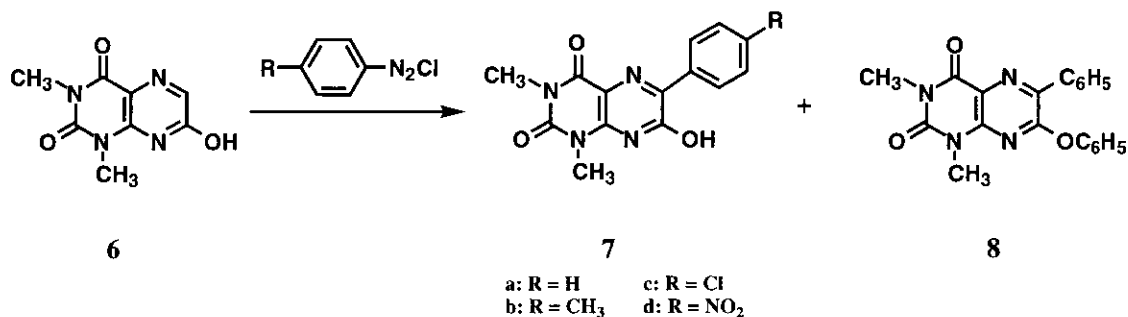
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**Abstract** – Reaction of 7-methoxy-1,3-dimethylumazine with benzenediazonium chloride in an alkaline aqueous solution afforded 6-phenyl- and 6-biphenyl-7-methoxy-1,3-dimethylumazines. Treatment of 7-dimethylamino-1,3-dimethylumazine with benzenediazonium chloride similarly gave the 6-phenyl and 6-biphenyl derivatives of the substrate together with 7-methylamino-6-phenyl-1,3-dimethylumazine. Analogous reactions of 7-substituted 1,3-dimethylumazines with several arenediazonium chlorides are described

Many of the naturally occurring and biologically important pteridine compounds possess a carbon functional group at the pyrazine moiety of pteridine ring. In general syntheses of such pteridines, the carbon functional group has been introduced at the step of pyrazine ring formation by employing an appropriate compound already carrying the functional group.<sup>1</sup> Direct introduction of a carbon substituent to pteridine ring by carbon-carbon bond formation looks straightforward and attractive. Among such reactions, homolytic C-acylation has been developed most widely to synthesize a variety of pteridine ketones.<sup>2-5</sup> Hydroxyalkyl groups are introduced by a similar manner.<sup>6</sup> Phenyl and several alkyl groups were introduced directly to some pteridines by a reaction with organolithium compounds or Grignard reagents.<sup>7-10</sup> We describe here a new method to introduce an aryl group directly to the pteridine ring by the action of arenediazonium salt in an alkaline solution.<sup>11</sup>



Treatment of 7-methoxy-1,3-dimethyl-illumazine (**1**) with benzenediazonium chloride in an aqueous solution adjusted at pH 9 – 10 at room temperature afforded 6-phenyl-7-methoxy-1,3-dimethyl-illumazine (**2a**) as the major product together with 6-biphenyl-7-methoxy-1,3-dimethyl-illumazine (**2e**). 4-Methyl-, 4-chloro-, and 4-nitrobenzenediazonium chlorides similarly reacted with **1** to give 6-(4-methylphenyl)-, 6-(4-chlorophenyl)-, and 6-(4-nitrophenyl)-7-methoxy-1,3-dimethyl-illumazines (**2b**, **2c**, and **2d**), respectively. The reaction of 7-dimethylamino-1,3-dimethyl-illumazine (**3**) with benzenediazonium chloride under similar conditions produced 6-phenyl-7-dimethylamino-1,3-dimethyl-illumazine (**4a**) and small amounts of 6-biphenyl-7-dimethylamino-1,3-dimethyl-illumazine (**4e**) and 6-phenyl-7-methylamino-1,3-dimethyl-illumazine (**5a**). The removal of a methyl group from the dimethylamino group was also observed in the reaction of **3** with 4-methyl- and 4-chlorobenzenediazonium chlorides. Namely, the reaction yielded 6-(4-methylphenyl)- and 6-(4-chlorophenyl)-7-dimethylamino-1,3-dimethyl-illumazines (**4b** and **4c**) as main products and 6-(4-methylphenyl)- and 6-(4-chlorophenyl)-7-methylamino-1,3-dimethyl-illumazines (**5b** and **5c**) as by-products, respectively. Reaction of 4-nitrobenzenediazonium chlorides with **3** gave 6-(4-nitrophenyl)-7-dimethylamino-1,3-dimethyl-illumazine (**4d**) in moderate yield.



7-Hydroxy-6-phenyl-1,3-dimethylimidazine (7a) was obtained as a major product together with 7-phenoxy-6-phenyl-1,3-dimethylimidazine (8) by the similar reaction of 7-hydroxy-1,3-dimethylimidazine (6) with benzenediazonium chloride. 4-Methyl-, 4-chloro-, and 4-nitrobenzenediazonium chlorides reacted analogously with 6 to yield the corresponding 6-arylation products (7b, 7c, and 7d). Similarly, 1,3,8-trimethylpteridine-2,4,7-trione (9) and 4-chlorobenzenediazonium chloride gave the arylated product (10). In the above reactions, no azo compounds were detected in contrast to a reported formation of an azo compound from 8-(D-ribityl)-2,4,7-pteridinetrione and 4-nitrobenzenediazonium chloride in an acetate buffer solution.<sup>12</sup> It is described that benzenediazonium salt produces phenyl radical in alkaline solution after a complex process.<sup>11</sup> Under the conditions employed in the above reactions, the arenediazonium chlorides probably decompose first into aryl radicals, which then react with 1,3-dimethylimidazines (1, 3, 6, and 9). The formation of biphenyl compounds (2e and 4e), methylamino compounds (5a, 5b, and 5c), and phenoxy compound (8) is best explained by a radical reaction mechanism.

## EXPERIMENTAL

Melting points are uncorrected. UV spectra were measured on a JASCO Ubest-55 spectrometer in methanol and expressed as  $\lambda_{\max}$  nm (log  $\epsilon$ ). <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were measured on a JEOL  $\alpha$ -

400 spectrometer in DMSO-*d*<sub>6</sub> unless otherwise mentioned and chemical shifts were expressed as  $\delta$ /ppm relative to internal tetramethylsilane.

*6-Phenyl- and 6-(4-biphenyl)-7-methoxy-1,3-dimethylumazines (2a, 2e)* A solution of benzenediazonium chloride, prepared from aniline (0.60 g, 6.5 mmol) and sodium nitrite (0.6 g, 8.7 mmol) in 2M HCl (50 mL), was added to a solution of 7-methoxy-1,3-dimethylumazine (0.45 g, 2.0 mmol) and sodium carbonate (9 g) in water (300 mL) at 5 °C. After being stirred at 5 °C for 1 h and then at rt overnight, the resulting mixture was extracted with dichloromethane (2 x 150 mL). The extract was subjected to chromatography on a silica gel column ( $\varnothing$  2 x 20 cm) eluted by a mixture of toluene and ethyl acetate (2:1, v/v) to give 6-phenyl-7-methoxy-1,3-dimethylumazine (**2a**) (0.25 g, 39%) and 6-(4-biphenyl)-7-methoxy-1,3-dimethylumazine (**2e**) (0.03 g, 4%).

**2a**: mp 182 – 183 °C (from toluene). Anal. Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>: C, 60.39; H, 4.13; N, 18.78. Found: C, 60.69; H, 4.34; N, 18.69. UV: 340 (4.21) and 284 (4.23). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.54 (s, 3H), 3.71(s, 3H), 4.18 (s, 3H), 7.41-7.50 (m, 3H), and 8.05-8.10 (m, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 28.80, 29.35, 54.99, 119.82, 128.25, 129.32, 129.57, 134.37, 139.67, 146.13, 151.09, 159.48, and 159.84.

**2e**: mp 254 – 255 °C (from toluene). Anal. Calcd for C<sub>21</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>: C, 67.37; H, 4.85; N, 14.96. Found: C, 67.35; H, 4.63; N, 14.80. UV: 354 (4.21), 296 (4.30), and 252 (4.04); <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.55(s, 3H), 3.73(s, 3H), 4.21(3, 3H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), and 8.20 (d, *J* = 8.3 Hz, 2H).

The following compounds were obtained in an analogous manner as above by the reactions of 7-methoxy- or 7-dimethylamino-1,3-dimethylumazine (**1, 3**) or 1,3,8-trimethylpteridine-2,4,7-trione (**9a**) with the diazonium salts prepared from the corresponding arylamines.

*6-(4-Methylphenyl)-7-methoxy-1,3-dimethylumazine (2b)* in 52% yield as colorless needles; mp 219 – 220 °C (from toluene). Anal. Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub>: C, 61.52; H, 5.17; N, 17.94. Found: C, 61.44; H, 5.18; N, 18.24. UV: 348 (4.14) and 285 (4.19); <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 2.41(s, 3H), 3.53 (s, 3H), 3.70 (s, 3H), 4.17 (s, 3H), 7.25 (d, *J* = 8.3 Hz, 2H), and 7.98 (d, *J* = 8.3 Hz, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 21.40, 28.78, 29.31, 54.94, 119.55, 128.98, 129.22, 131.53, 139.75, 143.02, 145.88, 151.10, 159.41, and 159.86.

*6-(4-Chlorophenyl)-7-methoxy-1,3-dimethylumazine (2c)* in 53% yield as pale yellow needles; mp 200 – 201 °C (from toluene). Anal. Calcd for C<sub>15</sub>H<sub>13</sub>ClN<sub>4</sub>O<sub>3</sub>: C, 54.14; H, 3.95; N, 16.84. Found: C, 54.39; H, 4.02; N, 16.63. UV: 347 (4.28) and 286 (4.29); <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.54 (s, 3H), 3.71(s, 3H), 4.19

(s, 3H), 7.42 (d,  $J = 8.8$  Hz, 2H), and 8.07 (d,  $J = 8.8$  Hz, 2H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 28.82, 29.38, 55.09, 119.69, 128.48, 130.60, 132.74, 135.72, 138.18, 146.23, 150.99, 159.34, and 159.69.

*6-(4-Nitrophenyl)-7-methoxy-1,3-dimethylumazine (2d)* in 49% yield as yellow needles; mp 243 – 244 °C (from toluene). Anal. Calcd for  $\text{C}_{15}\text{H}_{13}\text{N}_5\text{O}_5$ : C, 52.47; H, 3.82; N, 20.40. Found: C, 52.63; H, 3.82; N, 20.20. UV: 352 (4.19), 340 (4.17), and 245 (sh., 3.85);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 3.35 (s, 3H), 3.59 (s, 3H), 4.18 (s, 3H), 8.29 (d,  $J = 9.1$  Hz, 2H), and 8.38 (d,  $J = 9.1$  Hz, 2H).

*6-Phenyl-7-dimethylamino-1,3-dimethylumazine (4a)* in 59% yield as colorless needles; mp 175 °C (from methanol). Anal. Calcd for  $\text{C}_{16}\text{H}_{17}\text{N}_5\text{O}_2$ : C, 61.72; H, 5.50; N, 22.49. Found: C, 61.79; H, 5.43; N, 22.43. UV: 367 (4.10) and 300 (4.04);  $^1\text{H-NMR}$ : 2.91 (s, 6H), 3.29 (s, 3H), 3.53 (s, 3H), 7.42 (t,  $J = 7.3$  Hz, 1H), 7.48 (t,  $J = 7.3$  Hz, 2H), and 7.56 (d,  $J = 7.3$  Hz, 2H);  $^{13}\text{C-NMR}$ : 28.01, 28.64, 40.62, 115.57, 127.65, 128.24, 128.40, 136.84, 139.23, 145.60, 150.91, 154.51, and 159.31.

*6-(4-Biphenyl)-7-dimethylamino-1,3-dimethylumazine (4e)* in 7% yield as a by-product; mp 206 – 207 °C (from methanol). Anal. Calcd for  $\text{C}_{22}\text{H}_{21}\text{N}_5\text{O}_2$ : C, 68.21; H, 5.46; N, 18.08%. Found: C, 68.12; H, 5.18; N, 17.84. UV: 374 (4.21) and 310 (4.19);  $^1\text{H-NMR}$ : 2.96 (s, 6H), 3.30 (s, 3H), 3.54 (s, 3H), 7.40 (t,  $J = 7.3$  Hz, 1H), 7.50 (t,  $J = 7.3$  Hz, 2H), 7.67 (d,  $J = 8.3$  Hz, 2H), 7.75 (d,  $J = 7.3$  Hz, 2H), and 7.80 (d,  $J = 8.3$  Hz, 2H);  $^{13}\text{C-NMR}$ : 28.03, 28.66, 40.73, 115.77, 126.58, 126.62, 127.73, 128.22, 129.03, 136.37, 138.24, 139.39, 139.76, 145.57, 150.92, 154.59, and 159.31.

*6-Phenyl-7-methylamino-1,3-dimethylumazine (5a)* in 3% yield as another by-product; mp 334 °C (from toluene). Anal. Calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_5\text{O}_2$ : C, 60.80; H, 4.76; N, 23.64. Found: C, 60.59; H, 4.74; N, 23.85. UV: 352 (4.21) and 292 (4.05);  $^1\text{H-NMR}$ : 2.93 (s, 3H), 3.28 (s, 3H), 3.53 (s, 3H), and 7.48 – 7.61 (m, 5H);  $^{13}\text{C-NMR}$ : 27.93, 28.32, 28.56, 114.17, 128.51, 128.79, 129.01, 135.71, 137.91, 147.54, 150.92, 153.53, and 159.50.

*6-(4-Methylphenyl)-7-dimethylamino-1,3-dimethylumazine (4b)* in 42% yield as colorless leaflets; mp 199 – 200 °C (from toluene). Anal. Calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_5\text{O}_2$ : C, 62.74; H, 5.90; N, 21.53. Found: C, 63.04; H, 5.94; N, 21.48. UV: 371 (4.12) and 302 (3.99);  $^1\text{H-NMR}$ : 2.37 (s, 3H), 2.91 (s, 6H), 3.29 (s, 3H), 3.52 (s, 3H), 7.30 (d,  $J = 7.8$  Hz, 2H), and 7.47 (d,  $J = 7.8$  Hz, 2H);  $^{13}\text{C-NMR}$ : 20.88, 28.00, 28.61, 40.59, 115.55, 127.54, 128.95, 136.37, 136.95, 137.67, 145.47, 150.92, 154.56, and 159.34.

*6-(4-Methylphenyl)-7-methylamino-1,3-dimethylumazine (5b)* in 6% yield as a by-product as colorless leaflets; mp 321 – 323 °C, decomp (from toluene). Anal. Calcd for  $\text{C}_{16}\text{H}_{17}\text{N}_5\text{O}_2$ : C, 61.72; H, 5.50; N, 22.49. Found: C, 61.74; H, 5.34; N, 22.48. UV: 354 (4.00) and 293 (3.79);  $^1\text{H-NMR}$ : 2.41 (s, 3H),

3.50 (s, 3H), 3.69 (s, 3H), 5.73 (br. s, 1H), 7.29 (d,  $J = 7.8$  Hz, 2H), and 7.51 (d,  $J = 7.8$  Hz, 2H);  $^{13}\text{C-NMR}$ : 21.37, 28.43, 28.52, 28.94, 115.42, 128.46, 129.90, 132.42, 139.11, 139.61, 149.89, 151.54, 154.13, and 160.44.

*6-(4-Chlorophenyl)-7-dimethylamino-1,3-dimethylumazine (4c)* in 44% yield as colorless needles; mp 199 – 200 °C (from methanol). Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{ClN}_5\text{O}_2$ : C, 55.57; H, 4.67; N, 20.26. Found: C, 55.53; H, 4.75; N, 20.48. UV: 372 (4.08) and 304 (3.95);  $^1\text{H-NMR}$  2.92 (s, 6H), 3.29 (s, 3H), 3.52 (s, 3H), 7.55 (d,  $J = 8.3$  Hz, 2H), and 7.61 (d,  $J = 8.3$  Hz, 2H);  $^{13}\text{C-NMR}$ : 28.01, 28.66, 40.77, 115.78, 128.44, 129.48, 132.77, 135.44, 137.99, 145.68, 150.88, 154.47, and 159.22.

*6-(4-Chlorophenyl)-7-methylamino-1,3-dimethylumazine (5c)* as a by-product in 10% yield as colorless needles; mp 346 °C (from toluene). Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{ClN}_5\text{O}_2$ : C, 54.31; H, 4.25; N, 21.11; Found: C, 54.10; H, 4.14; N, 21.33. UV: 356 (4.00) and 293 (3.84);  $^1\text{H-NMR}$ : 2.93 (s, 3H), 3.28 (s, 3H), 3.54 (s, 3H), 7.50 (br. s, 1H), 7.57 (d,  $J = 8.8$  Hz, 2H), and 7.62 (d,  $J = 8.8$  Hz, 2H);  $^{13}\text{C-NMR}$ : 27.88, 28.20, 28.54, 114.22, 128.81, 130.43, 133.68, 134.61, 136.75, 147.70, 150.91, 153.59, and 159.39.

*6-(4-Nitrophenyl)-7-dimethylamino-1,3-dimethylumazine (4d)* in 67% yield as yellow needles; mp 222 – 223 °C (from toluene). Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_6\text{O}_4$ : C, 53.92; H, 4.53; N, 24.14. Found: C, 54.08; H, 4.52; N, 24.22. UV: 384 (4.16), 340 (sh., 4.02), 279 (sh., 4.04), and 251 (4.22);  $^1\text{H-NMR}$ : 2.94 (s, 6H), 3.29 (s, 3H), 3.53 (s, 3H), 7.88 (d,  $J = 8.3$  Hz, 2H), and 8.33 (d,  $J = 8.3$  Hz, 2H);  $^{13}\text{C-NMR}$ : 28.51, 29.18, 41.35, 116.73, 124.13, 129.30, 134.31, 145.95, 146.45, 147.16, 151.32, 154.88, 159.58.

*6-(4-Chlorophenyl)-1,3,8-trimethyl-2,4,7-pteridinetrione (10)* in 37% yield as yellow solid; mp 291 – 292 °C, decomp (from toluene). Anal. Calcd for  $\text{C}_{15}\text{H}_{13}\text{ClN}_4\text{O}_3$ : C, 54.14; H, 3.95; N, 16.34. Found: C, 54.31; H, 3.90; N, 16.32. UV: 369 (4.00), 301 (3.70), and 244 (3.86);  $^1\text{H-NMR}$ : 3.27 (s, 3H), 3.51 (s, 3H), 3.60 (s, 3H), 7.56 (d,  $J = 8.3$  Hz, 2H), and 8.27 (d,  $J = 8.3$  Hz, 2H);  $^{13}\text{C-NMR}$ : 28.16, 36.68, 37.85, 111.87, 128.14, 129.98, 134.05, 134.18, 141.76, 146.21, 151.64, 155.96, and 158.56.

*7-Hydroxy-6-phenyl-1,3-dimethylumazine (7a)* and *7-phenoxy-6-phenyl-1,3-dimethylumazine (8)* A solution of benzenediazonium chloride, prepared from aniline (0.56 g, 6 mmol) and sodium nitrite (0.6 g, 8.7 mmol) in 2M HCl (50 mL), was added to a solution of 7-hydroxy-1,3-dimethylumazine (0.42 g, 2.0 mmol) and sodium carbonate (9 g) in water (100 mL) at 5 °C. After being stirred at 5 °C for 1 h and then at rt overnight, the resulting mixture was shaken with dichloromethane (2 x 50 mL) to remove dark colored

material. The aqueous solution was adjusted to pH 4 with acetic acid and the precipitate was collected by filtration. The product was subjected to chromatography on a silica gel column ( $\varnothing$  2 x 20 cm) eluted by a mixture of dichloromethane and methanol (9:1, v/v) to give 7-hydroxy-6-phenyl-1,3-dimethylumazine (**7a**) (0.15 g, 30%) and 7-phenoxy-6-phenyl-1,3-dimethylumazine (**8**) (0.04 g, 6%).

**7a**: mp 344 °C (from methanol). Anal. Calcd for  $C_{14}H_{12}N_4O_3$ : C, 59.15; H, 4.25; N, 19.71. Found: C, 59.20; H, 4.05; N, 19.82. UV: 348 (4.19) and 282 (4.16);  $^1H$ -NMR: 3.32 (s, 3H), 3.52 (s, 3H), and 7.43-7.51 (m, 3H), and 8.05 – 8.07 (m, 2H);  $^{13}C$ -NMR: 28.21, 29.11, 118.45, 128.14, 128.60, 128.94, 135.11, 146.42, 150.64, 159.15, and 159.18.

**8**: mp 323 – 324 °C (from toluene). Anal. Calcd for  $C_{20}H_{16}N_4O_3$ : C, 66.66; H, 4.47; N, 15.55. Found: C, 66.72; H, 4.38; N, 15.33. UV: 356 (4.28) and 295 (4.36);  $^1H$ -NMR: 3.33 (s, 3H), 3.54 (s, 3H), 7.39 (t,  $J = 7.3$  Hz, 1H), 7.50 (t,  $J = 7.3$  Hz, 2H), 7.74 (d,  $J = 7.3$  Hz, 2H), 7.79 (d,  $J = 8.8$  Hz, 2H), 7.84 – 7.87 (m, 1H), and 8.22 (t,  $J = 8.8$  Hz, 2H);  $^{13}C$ -NMR: 28.06, 28.98, 126.22, 126.54, 127.12, 127.60, 128.86, 128.96, 134.15, 136.52, 138.34, 139.41, 140.33, 146.24, 150.51, and 159.07.

The following compounds were obtained in an analogous manner as above by the reactions of 7-hydroxy-1,3-dimethylumazine (**6**) and the diazonium salts prepared from the corresponding arylamines.

*7-Hydroxy-6-(4-methylphenyl)-1,3-dimethylumazine (7b)* in 15% yield: mp 264 – 265 °C (from methanol). Anal. Calcd for  $C_{15}H_{14}N_4O_3 \cdot 1/2H_2O$ : C, 58.63; H, 4.92; N, 18.23. Found: C, 58.92; H, 4.59; N, 18.23. UV: 352 (4.09) and 284 (4.08);  $^1H$ -NMR: 2.37 (s, 3H), 3.31 (s, 3H), 3.51 (s, 3H), 7.30 (d,  $J = 8.1$  Hz, 2H), and 7.99 (d,  $J = 8.1$  Hz, 2H);  $^{13}C$ -NMR: 20.91, 28.18, 29.07, 118.28, 128.48, 128.72, 132.34, 137.11, 138.52, 146.12, 150.60, 158.95, and 159.16.

*6-(4-Chlorophenyl)-7-hydroxy-1,3-dimethylumazine (7c)* in 36% yield: mp 350 – 351 °C (from methanol). Anal. Calcd for  $C_{14}H_{11}ClN_4O_3 \cdot 2/3H_2O$ : C, 50.83; H, 3.77; N, 16.94. Found: C, 50.92; H, 3.55; N, 16.75. UV: 351 (4.14) and 285 (4.10);  $^1H$ -NMR: 3.31 (s, 3H), 3.51 (s, 3H), 7.56 (d,  $J = 8.5$  Hz, 2H), and 8.12 (d,  $J = 8.5$  Hz, 2H);  $^{13}C$ -NMR: 28.18, 29.09, 118.35, 128.21, 130.20, 133.67, 133.95, 135.59, 146.52, 150.57, 159.02, and 159.07.

*7-Hydroxy-6-(4-nitrophenyl)-1,3-dimethylumazine (7d)* in 65 % yield: mp 309 – 310 °C (from methanol). Anal. Calcd for  $C_{14}H_{11}N_5O_5 \cdot 1/2H_2O$ : C, 46.68; H, 3.08; N, 19.44. Found: C, 46.46; H, 2.94; N, 19.17. UV: 392 (4.08), 315 (3.76), and 256 (sh., 3.94);  $^1H$ -NMR: 3.26 (s, 3H), 3.40 (s, 3H), 8.23 (d,  $J = 9.3$  Hz, 2H), and 8.72 (d,  $J = 9.3$  Hz, 2H);  $^{13}C$ -NMR: 27.63, 28.14, 110.51, 122.72, 128.63, 136.94, 145.05, 145.79, 150.19, 151.33, 159.37, and 165.40.

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