One-Pot Synthesis of Mannich Base Using Hydroxy Aromatic Rings and Secondary Amines

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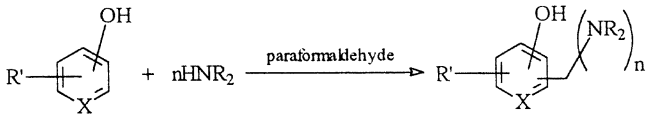
The aminoalkylation of aromatic substrates by the Mannich reaction is of considerable importance for the synthesis and modification of biologically active compounds.[1,2] It also provides a convenient access to many useful synthetic building blocks because the amino group can be easily converted into a variety of other functionalities.[3-5] It has been generally known that the reaction pathways of the Mannich reaction depend on the nucleophilicity of substrate and the pH of reaction medium.[6] Even though substituted phenols are commonly used in the Mannich reaction, it has been difficult to undergo aminomethylation of various phenols with sterically hindered amines. Instead of direct aminomethylation, bulky azacrown ethers were treated with the methanol solution of formaldehyde to provide the N-methoxymethyl-substituted azacrown ethers, which subsequently gave the Mannich bases by the reaction with a proper substrate.[7-9] However, a more convenient method[10] has been developed by Chi and co-workers using 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, paraformaldehyde and phenolic derivatives in benzene to produce double-armed diazacrown ethers in good yields without the isolation of intermediates. This successful one-pot reaction prompted us to study applicability of the same methodology to the aminomethylation of hydroxy heterocycles.

In this paper, we would like to report the result of one-pot Mannich reaction of secondary amines with hydroxy aromatic compounds in an aprotic solvent (Scheme 1). In particular, the relative reactivity and regioselectivity of hydroxypyridines have been examined in detail.



1 **2** **3**

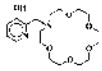
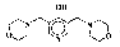
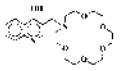
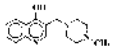
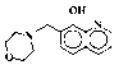
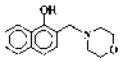
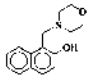
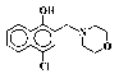
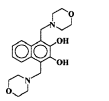
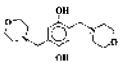
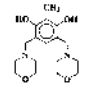
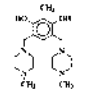
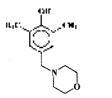
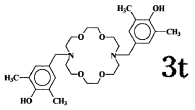
(X : N or C)

1		2
a 3-hydroxypyridine	**g** 2-naphthol	**a** morpholine
b 4-hydroxypyridine	**h** 4-chloro-1-naphthol	**b** pyrrolidine
c 2-hydroxypyridine	**i** 2,3-dihydroxynaphthalene	**c** 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane
d 4-hydroxyquinoline	**j** hydroquinone	
e 8-hydroxyquinoline	**k** 2-methylresorcinol	**d** 1,4,7,10,13-pentaoxa-16-azacyclooctadecane
f 1-naphthol	**l** 2,6-dimethylphenol	**e** N-methylpiperazine

Scheme 1

We started our study using 3-hydroxypyridine (**1a**) as a substrate for the Mannich reaction. Since pyridine is referred to as a π-deficient heterocycle,[11] hydroxypyridine would be expected as a deactivated nucleophile compared with phenol. However, **1a** was smoothly aminomethylated to give **3a** in 93% yield (Table 1). It is also underscored that the reaction is quite regioselective in providing **3a** without producing any other constitutional isomer. The formation of **3a** was confirmed by the ^{1}H NMR spectra in which all the hydrogens in the pyridine ring coupled each other. Usually, phenols are aminomethylated preferably at the ortho position,[12-16] which can be rationalized by a concerted mechanism.[17,18] The hydroxypyridine **1a** behaves very similarly to phenols, since the hydroxy group directs the Mannich reaction to occur at the ortho position, especially next to the nitrogen atom in the heterocycle.[19-21] The Mannich reaction of 4-hydroxypyridine (**1b**) also produced the ortho-substituted product **3d** in 46% yield. Treatment of pyrrolidine instead of morpholine under the same conditions gave similar results. In order to obtain double aminomethylation, 4-hydroxypyridine (**1b**) was treated with two equivalents of paraformaldehyde and morpholine in boiling p-xylene. To our surprise, 2-hydroxypyridine (**1c**) did not undergo aminomethylation under the same conditions. This fact might be ascribed to the prevailing keto form of **1c**, which has no phenolic acidic proton. Use of benzene instead of ethanol or p-xylene made no difference in the reaction. Our methodology was further applied to the more nucleophilic fused ring substrates (**1d-1i**). The Mannich reaction of hydroxyquinolines with various secondary amines provided the corresponding Mannich bases **3h**, **3j** and **3k** in 80-90% yields. It is interesting to note that the yield of **3k** relied on the reaction solvent used. When benzene was replaced with ethanol, the yield increased to 99%. The better result might be attributed to the decrease of intramolecular hydrogen bond of **1e** in the polar solvent. The positive outcome encouraged us to extend our investigation to the aminomethylation with a bulky secondary amine. But, the reaction of **1a** and **1d** with 1,4,7,10,13-pentaoxa-16-azacyclooctadecane produced **3c** and **3i**, respectively only in poor yields. The reason for the poor yields of **3c** and **3i** could be the steric hindrance of the bulky amino group in azacrown ether and the lower nucleophilicity of hydroxyheterocycles. The Mannich reaction of naphthols (**1f** and **1g**) was also tried and quantitatively produced the Mannich bases **3l** and **3m**. On the other hand, the reaction of

Table 1. Aminomethylation of various hydroxy aromatic compounds with secondary amines

Substrate 1	Amine 2	n	Product 3	Solvent	Isolated Yield (%)
1a	**2a**	1	 **3a**	benzene	93
1a	**2b**	1	 **3b**	benzene	90
1a	**2d**	1	 **3c**	benzene	17
1b	**2a**	1	 **3d**	benzene	46
1b	**2b**	1	 **3e**	benzene	56
1b	**2a**	2	 **3f**	p-xylene	26
1c	**2a**	1	 **3g**	benzene ethanol	0 0
1d	**2a**	1	 **3h**	benzene	95
1d	**2d**	1	 **3i**	benzene	12
1d	**2e**	1	 **3j**	benzene	98
1e	**2a**	1	 **3k**	benzene ethanol	71 99
1f	**2a**	1	 **3l**	benzene	99
1g	**2a**	1	 **3m**	benzene	99
1h	**2a**	1	 **3n**	benzene	70
1i	**2a**	2	 **3o**	benzene	81
1j	**2a**	2	 **3p**	benzene	45
1k	**2a**	2	 **3q**	benzene	89
1k	**2e**	2	 **3r**	benzene	86
1l	**2a**	1	 **3s**	benzene	94
1l	**2c**	0.5	 **3t**	benzene	75

4-chloro-1-naphthol (**1h**) which has an electron-withdrawing substituent produced **3n** in only 70% yield. The same procedure was also employed for the aminomethylation of dihydroxy aromatic compounds. With **1k**, the Mannich reaction was doubly activated by the two hydroxy groups and provided **3q** and **3r** in good yields even in the boiling benzene. In the case of **1l**, in which two ortho positions are already substituted by methyl groups, the aminomethylation occurred at the para position.

In summary, one-pot synthesis of Mannich bases with hydroxypyridines was effectively conducted and the reaction underwent regioselectively at the ortho position to alcohol group. Also, the reactivity of the Mannich reaction generally depended on the nucleophilicity of hydroxy aromatic rings. Studies are currently under way to examine the complexation between the possible host molecules **3** and various guests.

Experimental Section

Starting materials were purchased from Aldrich Chemical Company and used without further purification. All chromatography solvents were of analytical grade and freshly distilled prior to use. Thin layer chromatographic analyses were conducted by using pre-coated TLC plate (60 F_{254}, 20 cm × 20 cm) purchased from Merck Company. Silica gel (230-400 mesh) was used in flash chromatography and deactivated by *ca.* 2% triethylamine in eluent solution.

IR spectra were recorded on a Mattson 5000 (UNICAM) spectrometer (KBr). Melting points of the prepared compounds were determined on an Aldrich melt temp apparatus and uncorrected. ^{1}H and ^{13}C NMR (300 MHz, 75.48 MHz, respectively) spectra were recorded using a Varian Unityplus 300 FT NMR or Bruker AM-300 NMR spectrometer. Mass spectra were obtained using a KRATOS Profile HV-3 or Shimadzu GCMS-Q.P 5050 (70ev) spectrometer with a direct insertion probe.

The general experimental procedure. To a solution of hydroxy aromatic compound (1.05 mmol) and paraformaldehyde (36 mg, 1.26 mmol) in dry benzene (8 mL) was added the corresponding secondary amine (1.26 mmol) at room temperature. Then, the resulting mixture was heated at reflux for 18-22 hrs. The solvent was removed in vacuo and the crude product was purified by flash chromatography and/or recrystalization.

Preparation of 3f, 3o, 3p, 3q and 3r. To a solution of hydroxy aromatic compound (1.05 mmol) and paraformaldehyde (70 mg, 2.32 mmol) in dry benzene or p-xylene (20 mL) was added the corresponding secondary amine (2.32 mmol) at room temperature. The resulting solution was heated and purified as described in the general procedure.

Preparation of 3c and 3i. To a solution of hydroxy aromatic compound (0.45 mmol) and paraformaldehyde (13 mg, 0.45 mmol) in dry benzene (8 mL) was added 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (100 mg, 0.38 mmol) at room temperature. The resulting solution was heated and purified as described in the general procedure.

Preparation of 3t. To a solution of hydroxy aromatic compound (0.91 mmol) and paraformaldehyde (27 mg, 0.91 mmol) in dry benzene (8 mL) was added 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (100 mg, 0.38 mmol) at room temperature. The resulting solution was heated and purified as described in the general procedure. All the spectral data of new compounds are in accordance with the assigned structures of compounds **3a-3t**.

3-Hydroxy-2-(4′-morpholinylmethyl)pyridine (3a). light yellow solid; mp 94-95; ^{1}H NMR ($CDCl_3$) δ 2.64 (m, 4H), 3.75 (m, 4H), 3.93 (s, 2H), 7.12 (m, 2H), 8.04 (m, 1H), 10.62 (br. s, 1H); ^{13}C NMR ($CDCl_3$) δ 52.81, 63.81, 66.39, 122.84, 123.55, 139.96, 141.58, 153.85; IR (cm^{-1}) 3445, 3027, 1573, 1110, 863; MS *m z* (rel. intensity) 194 (M^+, 4), 192 (60), 161 (33), 133 (75), 109 (85), 85 (77), 79 (100), 66 (82), 54 (90).

3-Hydroxy-2-(1′-pyrrolidinylmethyl)pyridine (3b). colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.83 (m, 4H), 2.63 (m, 4H), 3.99 (s, 2H), 7.03 (m, 2H), 7.95 (m, 1H), 10.65 (br. s, 1H); ^{13}C NMR ($CDCl_3$) δ 23.61, 53.59, 60.90, 122.76, 123.39, 139.45, 143.12, 154.48; IR (cm^{-1}) 3425, 2973, 2838, 1576, 1273, 1449, 1102, 802; MS *m z* (rel. intensity) 178 (M^+, 5), 109 (100), 84 (15), 70 (30).

3-Hydroxy-2-[(1′,4′,7′,10′,13′-pentaoxa-16′-azacyclooctadecan-16′-yl)-methyl]pyridine (3c). brown liquid; ^{1}H NMR (CD_3OD) δ 2.69 (m, 4H), 3.44-3.76 (m, 22H), 7.01 (m, 2H), 7.78 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 54.12, 69.75, 70.11, 70.40, 70.48, 70.54, 71.12, 123.99, 139.12, 139.66, 154.57, 207.11; IR (cm^{-1}) 3436, 2955, 2851, 1573, 1418; MS *m z* (rel. intensity) 370 (M^-, 8), 309 (3), 262 (100), 232 (8), 176 (10), 109 (64), 56 (18), 45 (20).

4-Hydroxy-2-(4′-morpholinylmethyl)pyridine (3d). light yellow liquid; ^{1}H NMR ($CDCl_3$) δ 2.53 (t, J = 4.1 Hz, 4H), 3.57 (s, 2H), 3.70 (t, J = 4.5Hz, 4H), 6.56 (d, J = 6.3 Hz, 1H), 7.91 (m, 2H); ^{13}C NMR (CD_3OD) δ 54.54, 55.25, 67.77, 117.93, 126.16, 139.05, 139.52, 180.42; IR (cm^{-1}) 3415, 3244, 1922, 1641, 1393, 1530, 1114, 836; MS *m z* (rel. intensity) 194 (M^+, 78), 163 (31), 135 (35), 108 (100), 84 (75), 56 (22), 47 (18).

4-Hydroxy-2-(1′-pyrrolidinylmethyl)pyridine (3e). reddish liquid; ^{1}H NMR ($CDCl_3$/CD_3OD) δ 1.72 (m, 4H), 2.54 (m, 4H), 3.59 (s, 2H), 6.43 (d, J = 6.5 Hz, 1H), 7.72 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 23.55, 53.57, 55.30, 112.35, 119.92, 146.35, 148.16, 167.18; IR (cm^{-1}) 3430, 1394, 1641, 1168, 836, 547; MS *m z* (rel. intensity) 179 (M^-+1, 27), 178 (M^+, 100), 149 (22), 135 (12), 108 (61), 84 (79), 70 (91), 47 (16).

4-Hydroxy-3,5-bis(4′-morpholinylmethyl)pyridine (3f). white solid; mp 173-174 °C; ^{1}H NMR ($CDCl_3$) δ 2.54 (m, 8H), 3.63 (s, 4H), 3.74 (t, J = 4.5 Hz, 8H), 8.20 (m, 2H); ^{13}C NMR (CD_3OD) δ 54.54, 55.41, 67.71, 124.94, 138.96, 178.92; IR (cm^{-1}) 3435, 3059, 2850, 1642, 1559, 1499, 1271, 1116, 865, 768; MS *m z* (rel. intensity) 294 (M^++1, 14), 293 (M^-, 46), 264 (13), 235 (45), 206 (100), 177 (35), 148 (55), 121 (65), 86 (64), 66 (39), 56 (47).

4-Hydroxy-3-(4′-morpholinylmethyl)quinoline (3h). yellow solid; mp 78-80 °C; ^{1}H NMR ($CDCl_3$) δ 2.51 (t, J = 6.7 Hz, 4H), 3.50 (s, 2H), 3.64 (t, J = 8.2 Hz, 4H), 7.34 (m, 1H), 7.61 (m, 2H), 8.03 (s, 1H), 8.38 (m, 1H); IR (cm^{-1}) 3454, 3063, 2922, 2854, 1623, 1581, 1518; MS *m z* (rel. intensity) 245 (M^-+1, 15), 244 (M^-, 100), 171 (10), 158 (90), 130 (26), 102 (34), 87 (74), 77 (27), 57 (84).

4-Hydroxy-3-[(1′,4′,7′,10′,13′-pentaoxa-16′-azacyclooctadecan-16′-yl)-methyl]quinoline (3i). white solid; mp 129-131 °C; ^{1}H NMR ($CDCl_3$) δ 2.73 (m, 4H), 3.55 (m, 22H), 7.24-8.47 (m, 5H); IR (cm^{-1}) 3454, 2885, 1623, 1573, 1493; MS *m z* (rel. intensity) 420 (M^+, 1), 418 (1), 302 (70), 232 (10), 159 (100), 145 (52), 130 (98), 102 (34), 89 (50), 77 (44), 58 (94).

4-Hydroxy-3-(4′-methyl-1′-piperazinylmethyl)quinoline (3j). white solid; mp 213-214 °C; ^{1}H NMR (MeOH) δ 2.21 (s, 3H), 2.43 and 2.59 (m, 8H), 3.58 (s, 2H), 7.38-8.34 (m, 5H); IR (cm^{-1}) 3450, 2943, 2789, 1623, 1571, 1501; MS *m z* (rel. intensity) 257 (M^+, 55), 186 (32), 171 (10), 158 (44), 130 (14), 99 (50), 77 (19), 58 (100).

8-Hydroxy-7-(4′-morpholinylmethyl)quinoline (3k). dark brown liquid; ^{1}H NMR ($CDCl_3$) δ 2.62 (t, J = 6.6 Hz, 4H), 3.77 (t, J = 7.1 Hz, 4H), 3.87 (s, 2H), 7.28 (m, 2H), 7.38 (m, 1H), 8.09 (m, 1H), 8.85 (m, 1H); IR (cm^{-1}) 3363, 3067, 2954, 2854, 1115; MS *m z* (rel. intensity) 244 (M^+, 3), 186 (11), 171 (14), 159 (100), 130 (21), 84 (55), 77 (19), 56 (9).

2-(4′-Morpholinylmethyl)-1-naphthol (3l). reddish liquid; ^{1}H NMR ($CDCl_3$) δ 2.6 (m, 4H), 3.76 (t, J = 7.0 Hz, 4H), 3.82 (s, 2H), 7.05 (m, 1H), 7.29 (m, 1H), 7.44 (m, 2H), 7.74 (m, 1H), 8.23 (1H); MS *m z* (rel. intensity) 244 (M^++1, 33), 243 (M^+, 97), 170 (15), 157 (55), 128 (67), 102 (20), 86 (100), 77 (22), 57(99).

1-(4′-Morpholinylmethyl)-2-naphthol (3m). white solid; mp 113-115 °C; ^{1}H NMR ($CDCl_3$) δ 2.68 (4H), 3.8 (t, J = 6.9 Hz, 4H), 4.16 (s, 2H), 7.09 (m, 1H), 7.30 (m, 1H), 7.45 (m, 1H), 7.76 (m, 3H); IR (cm^{-1}) 3455, 3061, 2959, 1116; MS *m z* (rel. intensity) 244 (M^++1, 13), 243 (M^-, 70), 170 (7), 157 (56), 128 (85), 86 (100), 57 (90).

4-Chloro-2-(4′-morpholinylmethyl)-1-naphthol (3n). reddish liquid; ^{1}H NMR ($CDCl_3$) δ 2.59 (m, 4H), 3.76 (m, 6H), 7.16 (s, 1H), 7.53 (m, 2H), 8.19 (m, 2H); IR (cm^{-1}) 3397, 3048, 2980, 1117; MS *m z* (rel. intensity) 277 (M^-, 79), 279 (M^-+2, 47), 190 (60), 162 (44), 127 (56), 101 (31), 87 (100), 77 (34), 57 (91).

2,3-Dihydroxy-1,4-bis(4′-morpholinylmethyl)naphthalene (3o). colorless liquid; ^{1}H NMR (CD_3OD) δ 2.51 (m, 8H), 3.57 (m, 8H), 3.98 (s, 4H), 7.18 (m, 2H), 7.80 (m, 2H); ^{13}C NMR (CD_3OD) δ 54.51, 56.37, 67.99, 113.55, 124.07, 124.53, 129.28, 147.58; MS *m z* (rel. intensity) 358 (M^+, 7), 356 (27), 269 (73), 217 (26), 182 (94), 154 (87), 127 (100), 86 (60), 59 (75).

2,5-Bis(4′-morpholinylmethyl)hydroquinone (3p). brown solid; mp 188-191 °C; ^{1}H NMR (CD_3OD) δ 2.39 (m, 8H), 3.47 (s, 4H), 3.56 (m, 8H), 6.44 (s, 2H); ^{13}C NMR (CD_3OD) δ 54.53, 61.19, 67.99, 117.76, 123.13, 150.84; IR (cm^{-1}) 3518, 3479, 2961, 2841, 1455, 1021, 1654, 1233; MS *m z* (rel. intensity) 445 (M^-+1, 5), 444 (M^+, 18), 351 (8), 277 (35), 219 (45), 165 (27), 147 (59), 113 (48), 96 (73), 82 (75), 71 (92), 5 (100).

2-Methyl-4,6-bis(4′-morpholinylmethyl)resorcinol (3q).

white solid: mp 193-195 °C; ^{1}H NMR ($CDCl_3$) δ 2.1 (s, 3H), 2.53 (m, 8H), 3.57 (s, 4H), 3.73 (t, J = 6.6 Hz, 8H), 6.43 (OH, 2H), 7.23 (1H); IR (cm^{-1}) 3453, 2954, 2825, 1623, 1114; MS m/z (rel. intensity) 322 (M^+, 48), 235 (100), 149 (26), 121 (12), 86 (50), 57 (34).

2-Methyl-4,6-bis(4′-methyl-1′-piperazinylmethyl)resorcinol (3r). light brown solid: mp 144-145 °C; ^{1}H NMR ($CDCl_3$) δ 2.1 (s, 3H), 2.3 (s, 6H), 2.37-2.65 (m, 16H), 3.58 (s, 4H), 6.43 (s, 1H); IR (cm^{-1}) 3453, 2938, 2834, 1618, 1458, 1342; MS m/z (rel. intensity) 348 (M^+, 30), 248 (78), 177 (15), 99 (70), 70 (32), 58 (100).

2,6-Dimethyl-4-(4′-morpholinylmethyl)phenol (3s). yellow liquid; ^{1}H NMR (CD_3OD) δ 2.17 (s, 6H), 2.33 (t, J = 4.5 Hz, 4H), 3.33 (s, 2H), 3.59 (t, J = 4.7 Hz, 4H), 6.82 (m, 2H); ^{13}C NMR (CD_3OD) δ 16.69, 54.49, 64.05, 67.87, 125.4, 128.6, 130.9, 153.7; IR (cm^{-1}) 3451, 3391, 2862, 2963, 1652, 1213, 1156, 1018; MS m/z (rel. intensity) 221 (M^+, 12), 218 (75), 188 (70), 146 (78), 134 (99), 99 (79), 85 (100), 76 (75), 55 (91).

7,16-Bis[(3′,5′-dimethyl-4′-hydroxyphenyl)methyl]-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (3t). white solid: mp 100-102 °C; ^{1}H NMR (CD_3OD) δ 2.25 (m, 12H), 2.83 (t, J = 6.0 Hz, 8H), 3.52 (s, 4H), 3.64-3.69 (m, 16H), 6.94 (m, 4H); ^{13}C NMR (CD_3OD) δ 10.68, 48.83, 54.72, 64.85, 65.76, 119.56, 124.58, 125.14, 147.4; IR (cm^{-1}) 3466, 3209, 1668, 1224; MS m/z (rel. intensity) 530 (M^+, 1), 425 (10), 397 (48), 291 (51), 263 (98), 163 (45), 135 (100), 91 (5).

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