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One-pot three-component solvent-free synthesis of 1-[(1,3-thiazol-2-ylamino)methyl]-2-naphthols

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Abstract

A series of 1-[(1,3-thiazol-2-ylamino)methyl]-2-naphthols were synthesized via one-pot three-component Mannich reaction of 2-aminothiazoles, aldehydes and 2-naphthol under solvent-free conditions. This protocol has advantages of no use of volatile organic solvents and hazardous catalysts. Work-up procedure is simple and yields are high.

Keywords: aldehyde; heteroarylamine; Mannich reaction; multicomponent synthesis; 2-naphthol.

Introduction

The Mannich reaction is one of the most important C-C bond formation reactions in organic synthesis. Its products (Mannich bases) are of considerable importance in industry, natural products, chemistry, and pharmacy (Azend et al., 1998). A large number of studies on the Mannich-type reactions have been reported (Gu et al., 2008; Uraguchi et al., 2008; Bayrak et al., 2009; Candeias et al., 2009; Hong et al., 2009; Odedra and Seeberger, 2009) with many methods utilizing Lewis acids (Ollevier and Nadeau, 2007; Stas and Tehrani, 2007; Wang et al., 2007b; Wu et al., 2007b; Ramalingam and Kumar, 2008; Sanjeeva and Purnachandra, 2008; Chen et al., 2009), Bronsted acids (Guo et al., 2007; Rueping et al., 2007; Yamanaka et al., 2007), solid acids (Bigdeli et al., 2007; Li et al., 2007; Wang et al., 2007a,c; Reddy et al., 2008), bases (Chandler et al., 2009; Wu et al., 2009), metal complexes (Wu et al., 2007a; Wieland et al., 2009), ionic liquids (Dong et al., 2007; Fang et al., 2009), inorganic salts (Aryanasab and Saidi, 2008; Kidwai et al., 2008), and organic compounds (Verkade et al., 2008; Kano et al., 2009) as catalysts and many volatile organic solvents, some of which are hazardous for the environment. There are few reports on the use of heteroarylamines as substrates in the Mannich-type reactions (Shaabani et al., 2007; Hao et al., 2009).

In this paper, we report one-pot three-component Mannich-type reactions of heteroarylamines, 2-aminothiazoles, with aldehydes and 2-naphthol under solvent- and catalyst-free conditions to synthesize a series of novel 1-[(1,3-thiazol-2-ylamino)methyl]-2-naphthols.

Results and discussion

Initially, the model Mannich reaction of 2-aminothiazole, benzaldehyde, and 2-naphthol was attempted (Scheme 1) under different conditions. This reaction was tested under catalyst-free conditions in different solvents. It was found that the reactions in organic solvents including acetonitrile, methanol, ethanol, acetic acid, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and dichloromethane did not afford any products. The reaction in water gave the product **1a** in low yield. The use of many catalytic systems did not provide any advantage. However, the reaction under solvent-free conditions gave the product **1a** in high yield. The best yield was obtained by conducting the reaction at 120°C for 6 h.

The scope and limitations of these Mannich-type reactions was studied (Table 1). It was found that aromatic aldehydes bearing electron donating group such as $-OCH_3$ are more reactive than the aldehydes with electron-withdrawing groups such as $-NO_2$ or -Cl. The use of aliphatic aldehydes in comparison to aromatic aldehydes results in much faster reaction rates and higher yields. The reactions using phenols other than 2-naphthol, such as phenol, 4-methylphenol, 4-methoxyphenol, 2-chlorophenol, 1-naphthol, 5-quinolinol, and 8-quinolinol were also tested. However, only traces of the desired products were obtained with these substrates under similar conditions.

Conclusion

One-pot three-component Mannich reaction of 2-aminothiazoles, aldehydes, and 2-naphthol under solvent- and catalyst-free conditions was developed. A series of 1-[(1,3-thiazol-2-ylamino)methyl]-2-naphthols was synthesized. The developed protocol does not use volatile organic solvents and hazardous catalysts.

Experimental

IR spectra were recorded using KBr pellets on a Digilab FTS 3000 FTIR spectrophotometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Mercury Plus-400 instrument using DMSO-d_6 as solvent and Me_4Si as internal standard. Elemental analyses were performed on a Vario E1 Elemental Analysis instrument. Mass spectra were recorded on a QP-1000A GC-MS using the electron impact mode (70 eV). Melting points were obtained using an electrothermal melting point apparatus. Aldehydes and 2-naphthol were purified by distillation or crystallization. 2-Aminothiazoles were prepared according to the literature method of Balalaie et al. (2008).

Table 1 Synthesis of 1-[(1,3-thiazol-2-ylamino)methyl]-2-naphthols by one-pot three-component Mannich reactions.

Product	R^1	R^2	Time (h)	Yield (%)[a]	mp. (°C)
1a	H	C_6H_5-	6	89	196–198
1b	H	2-$CH_3OC_6H_4$-	7	92	152–154
1c	H	4-$CH_3OC_6H_4$-	7	95	158–160
1d	H	2-ClC_6H_4-	10	76	180–182
1e	H	4-ClC_6H_4-	8	85	170–171
1f	H	3-$NO_2C_6H_4$-	9	78	181–183
1g	H	4-OHC_6H_4-	10	75	200–202
1h	H	4-OH-3-$CH_3OC_6H_3$-	10	72	160–162
1i	H		7	96	168–169
1j[b]	H	CH_3CH_2-	6	94	183–184
1K[c]	H	$CH_3CH_2CH_2$-	6	96	171–172
1l[b]	C_6H_5	CH_3CH_2-	8	88	170–172

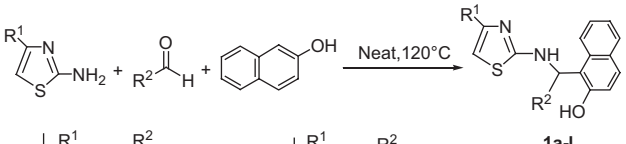
[a]Yields refer to the isolated products.
[b]The reactions were carried out at reflux condition (48°C).
[c]The reactions were carried out at reflux condition (76°C).

General procedure for the synthesis of 1-[(1,3-thiazol-2-ylamino)methyl]-2-naphthols

A mixture of a 2-aminothiazole (1 mmol), an aldehyde (1 mmol), and 2-naphthol (1 mmol) was heated at 120°C except for propanal (48°C) and butanal (76°C) for the period of time indicated below. Then the resultant solid was crystallized from acetone to give product **1a-l** as white crystals.

1-[Phenyl(1,3-thiazol-2-ylamino)methyl]-2-naphthol (1a) Reaction time 6 h; yield 89%; mp 196–198°C; IR: 3381, 1599, 1542, 1515, 1433 cm^{-1}; ^1H NMR: δ 10.10 (s, 1H), 8.24 (s, 1H), 7.91–7.10 (m, 13H), 6.42 (d, *J*=4.0 Hz, 1H); ^{13}C NMR: δ 168.9, 157.7, 153.1, 144.7, 138.3, 134.0, 131.8, 129.3, 128.3, 128.0, 126.5, 122.6, 122.5, 122.4, 119.2, 118.5, 107.4, 54.7; MS: *m/z* 332 (M^+). Anal. Calcd for $C_{20}H_{16}N_2OS$: C, 72.26; H, 4.85; N, 8.43. Found: C, 72.11; H, 4.83; N, 8.40.

1-[(2-Methoxyphenyl)(1,3-thiazol-2-ylamino)methyl]-2-naphthol (1b) Reaction time 7 h; yield 92%; mp 152–154°C; IR: 3352, 3123, 1624, 1539, 1434, 1247, 1157, 1047, 1027, 741 cm^{-1}; ^1H NMR: δ 10.14 (s, 1H), 8.35 (s, 1H), 7.94–6.93 (m, 12H), 6.53 (d, *J*=4.0 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR: δ 168.8, 158.1, 153.3, 138.4, 134.7, 133.5, 129.6, 128.8, 128.6, 127.3, 127.0, 122.6, 122.5, 121.9, 119.3, 118.2, 117.4, 114.4, 107.1, 54.1, 53.7; MS: *m/z* 362 (M^+). Anal. Calcd for $C_{21}H_{18}N_2O_2S$: C, 69.59; H, 5.01; N, 7.73. Found: C, 69.71; H, 5.00; N, 7.75.



	R^1	R^2
1a	H	C_6H_5
1b	H	2-$CH_3OC_6H_4$
1c	H	4-$CH_3OC_6H_4$
1d	H	2-ClC_6H_4
1e	H	4-ClC_6H_4
1f	H	3-$O_2NC_6H_4$

	R^1	R^2
1g	H	4-HOC_6H_4
1h	H	4-HO-3-$CH_3OC_6H_3$
1i	H	
1j	H	CH_3CH_2
1k	H	$CH_3CH_2CH_2$
1l	C_6H_5	CH_3CH_2

Scheme 1 Synthesis of 1-[(1,3-thiazol-2-ylamino)methyl]-2-naphthols.

1-[(4-Methoxyphenyl)(1,3-thiazol-2-ylamino)methyl]-2-naphthol (1c) Reaction time 7 h; yield 95%; mp 158–160°C; IR: 3352, 3127 1610, 1542, 1509, 1454 cm^{-1}; ^1H NMR: δ 10.13 (s, 1H), 8.33 (s, 1H), 7.92–6.80 (m, 12H), 6.59 (d, *J*=4.0 Hz, 1H), 3.68 (s, 3H); ^{13}C NMR: δ 168.9, 157.7, 153.0, 138.2, 134.3, 132.1, 129.2, 128.6, 128.5, 127.5, 126.0, 122.4, 122.3, 119.3, 118.5, 113.4, 107.4, 54.9, 53.3; MS (EI): *m/z* 362 (M^+). Anal. Calcd for $C_{21}H_{18}N_2O_2S$: C, 69.59; H, 5.01; N, 7.73. Found: C, 69.29; H, 5.00; N, 7.70.

1-[(2-Chlorophenyl)(1,3-thiazol-2-ylamino)methyl]-2-naphthol (1d) Reaction time 10 h; yield 76%; mp 180–182°C. IR: 3352, 1630, 1538, 1454 cm^{-1}; ^1H NMR: δ 10.25 (s, 1H), 8.33 (s, 1H), 7.92–7.27 (m, 12H), 6.52 (d, *J*=4.0 Hz, 1H); ^{13}C NMR: δ 168.8, 157.7, 154.7, 142.1, 138.4, 132.6, 130.7, 129.2, 128.9, 128.8, 128.5, 127.6, 126.5, 122.4, 122.3, 119.3, 118.5, 113.5, 107.5, 53.2; MS (EI): *m/z* 366 (M^+). Anal. Calcd for $C_{20}H_{15}ClN_2OS$: C, 65.48; H, 4.12; N, 7.64. Found: C, 65.52; H, 4.13; N, 7.66.

1-((4-Chlorophenyl)(1,3-thiazol-2-ylamino)methyl)-2-naphthol (1e) Reaction time 8 h; yield: 85%; mp 170–171°C; IR: 3389, 3122, 2924, 1626, 1536, 1511, 1435, 1332, 1269, 815 cm^{-1}; ^1H NMR: δ 10.22 (s, 1H), 8.15 (s, 1H), 7.84–6.99 (m, 12H), 6.70 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR: δ 168.8, 157.7, 154.7, 153.1, 138.4, 130.7, 129.2, 128.9, 128.8, 128.5, 126.3, 122.3, 122.2, 119.3, 118.5, 112.2, 108.4, 53.2; MS: m/z 366 (M^+). Anal. Calcd for $C_{20}H_{15}ClN_2OS$: C, 65.48; H, 4.12; N, 7.64. Found: C, 65.41; H, 4.10; N, 7.62.

1-[(3-Nitrophenyl)(1,3-thiazol-2-ylamino)methyl]-2-naphthol (1f) Reaction time 9 h; yield 78%; mp 181–183°C; IR: 3368, 3125, 1624, 1535, 1444 cm^{-1}; ^1H NMR: δ 10.26 (s, 1H), 8.51–8.04 (m, 3H), 7.90 (s, 1H), 7.83–7.02 (m, 9H), 6.68 (d, *J*=3.6 Hz, 1H); ^{13}C NMR: δ 168.6, 153.2, 145.8, 138.3, 138.2, 132.9, 132.0, 130.0, 129.6, 128.7, 128.5, 126.6, 123.3, 122.6, 121.3, 120.6, 118.4, 118.2, 107.4, 53.1; MS: *m/z* 377 (M^+). Anal. Calcd for $C_{20}H_{15}N_3O_3S$: C, 63.65; H, 4.01; N, 11.13. Found: C, 63.52; H, 4.03; N, 11.10.

1-[(4-Hydroxyphenyl)(1,3-thiazol-2-ylamino)methyl]-2-naphthol (1g) White crystal. Reaction time: 10 h. Yield: 75%; mp 200–202°C; IR: 3384, 3129, 1626, 1535, 1444 cm^{-1}; ^1H NMR: δ 10.13 (s, 1H), 8.35 (s, 1H), 7.90 (s, 1H), 7.79–6.98 (m, 12H), 6.60 (d, *J*=3.6 Hz, 1H); ^{13}C NMR: δ 168.9, 153.0, 142.7, 138.2, 132.3, 129.2, 128.6, 128.4, 128.3, 127.9, 126.1, 126.0, 124.0, 122.3, 119.2, 118.4, 106.7, 53.5; MS: *m/z* 348 (M^+). Anal. Calcd for $C_{20}H_{16}N_2O_2S$: C, 68.94; H, 4.63; N, 8.04. Found: C, 68.81; H, 4.62; N, 8.05.

1-[(4-Hydroxy-3-methoxyphenyl)(1,3-thiazol-2-ylamino)methyl]-2-naphthol (1h) Reaction time 10 h; yield 72%; mp 160–162°C; IR: 3383, 3127, 1623, 1531, 1442 cm^{-1}; ^1H NMR: δ 10.28 (s, 1H), 8.37 (s, 1H), 7.92 (s, 1H), 7.84–6.80 (m, 11H), 6.59 (d, *J*=4.0 Hz, 1H), 3.68 (s, 3H); ^{13}C NMR: δ 168.6, 153.2, 145.8, 138.3, 132.9, 132.0, 130.0, 129.6, 128.7, 128.5, 126.6, 123.3, 122.6, 122.5, 121.3, 120.6, 118.4, 118.2, 106.4, 55.6, 53.1. MS: *m/z* 378 (M^+). Anal. Calcd for $C_{21}H_{18}N_2O_3S$: C, 66.65; H, 4.79; N, 7.40. Found: C, 66.75; H, 4.81; N, 7.37.

1-[Furan-2-yl(1,3-thiazol-2-ylamino)methyl]-2-naphthol (1i) Reaction time 7 h; yield 96%; mp 168–169°C; IR: 3345, 3129, 1627, 1559, 1440, 1338 cm^{-1}; ^1H NMR: δ 10.20 (s, 1H), 8.44 (s, 1H), 8.06–7.70 (m, 9H), 6.59 (d, *J*=4.0 Hz, 1H), 6.37–6.18 (m, 2H); ^{13}C NMR: δ 168.3, 154.7, 153.3, 141.8, 141.7, 138.2, 132.4, 129.5, 128.5, 126.1, 123.4, 122.4, 118.5, 116.7, 110.4, 106.9, 106.4, 49.1; MS: *m/z* 322 (M^+). Anal. Calcd for $C_{18}H_{14}N_2O_2S$: C, 67.06; H, 4.38; N, 8.69. Found: C, 67.13; H, 4.39; N, 8.66.

1-[1-(1,3-Thiazol-2-ylamino)propyl]-2-naphthol (1j) Reaction time 6 h; yield 94%; mp 183–184°C; IR: 3388, 3233, 1622, 1535, 1350 cm^{-1}; ^1H NMR: δ 10.01 (s, 1H), 7.98 (s, 1H), 7.90–7.01 (m, 8H), 4.55 (d, *J*=4.0 Hz, 1H), 1.86–1.80 (m, 2H), 1.04 (t, *J*=7.2 Hz, 3H); ^{13}C NMR: δ 168.2, 156.7, 152.7, 138.9, 129.6, 128.8, 128.2, 123.9, 122.7, 122.6, 119.3, 118.4, 107.4, 56.1, 30.2, 10.3; MS: *m/z* 284 (M^+). Anal. Calcd for $C_{16}H_{16}N_2OS$: C, 67.58; H, 5.67; N, 9.85. Found: C, 67.47; H, 5.66; N, 9.81.

1-[1-(1,3-Thiazol-2-ylamino)butyl]-2-naphthol (1k) Reaction time 6 h; yield 96%; mp 171–172°C; IR: 3386, 3231, 1620, 1532, 1349 cm^{-1}; ^1H NMR: δ 10.08 (s, 1H), 8.02 (s, 1H), 8.00–7.06 (m, 8H), 4.22 (d, *J*=4.0 Hz, 1H), 3.02–2.98 (m, 2H), 1.21–1.19 (m, 2H), 1.02 (t, *J*=7.2 Hz, 3H); ^{13}C NMR: δ 168.0, 156.9, 151.1, 139.2, 129.6, 128.5, 128.2, 123.2, 123.1, 121.7, 119.8, 117.5, 107.2, 56.9, 50.5, 17.3, 14.2; MS: *m/z* 298 (M^+). Anal. Calcd for $C_{17}H_{18}N_2OS$: C, 68.42; H, 6.08; N, 9.39. Found: C, 68.36; H, 6.09; N, 9.42.

1-[1-(4-Phenyl-1,3-thiazol-2-ylamino)propyl]-2-naphthol (1l) Reaction time 8 h; Yield 88%; mp 170–172°C; IR: 3390, 3237, 1625, 1537, 1354 cm^{-1}; ^1H NMR: δ 10.13 (s, 1H), 8.33 (s, 1H), 8.03–7.15 (m, 12H), 4.22 (d, *J*=4.0 Hz, 1H), 1.83–1.81 (m, 2H), 1.04 (t, *J*=7.2 Hz, 3H); ^{13}C NMR: δ 169.7, 156.7, 152.7, 144.1, 138.9, 135.1, 129.6, 129.0, 128.8, 128.4, 128.2, 123.9, 122.7, 122.6, 119.3, 118.4, 112.3, 56.5, 31.9, 10.1; MS: *m/z* 360 (M^+). Anal. Calcd for $C_{22}H_{20}N_2OS$: C, 73.30; H, 5.59; N, 7.77. Found: C, 73.12; H, 5.58; N, 7.78.

Acknowledgments

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