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Article

One-pot synthesis of 1-amidoalkyl-2-naphthols catalyzed by melamine-Br_3 under solvent-free conditions

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ABSTRACT

A facile and efficient method has been developed for the synthesis of 1-amidoalkyl-2-naphthols *via* the one-pot multi-component condensation of 2-naphthol with aromatic aldehydes and acetamide or thioacetamide in the presence of melamine-Br_3 under solvent-free conditions. There are several advantages to this reaction, including high yields, short reaction time, and high catalytic efficiency.

1. Introduction

Multi-component reactions (MCRs), where three or more reactants are combined into a one-pot process, represent an increasingly important and attractive area of research in organic synthesis because they provide high levels of efficiency via the combination of several operational steps, as well as allowing for operational steps involving the isolation of intermediates or changing of reaction conditions to be avoided. In terms of the advantages that they offer, MCRs are general efficient procedures that provide high levels of atom economy and significant cost savings. The discovery and development of novel and known MCRs have consequently become a popular area of research in organic chemistry.

Compounds containing 1,3-amino-oxygenated functional groups are frequently used as biologically active natural products, and this structural motif can also be found in a number of potent drugs such as nucleoside antibiotics and the HIV protease inhibitors [1,2], such as ritonavir and liponavir [3,4]. 1-Amidoalkyl-2-naphthol derivatives can be converted to 1-aminomethyl-2-naphthols via an amide hydrolysis reaction. These compounds are important synthetic building blocks and exhibit a range of biological activity, including depressive and bradycardia effects in humans [4,5].

1-Amidoalkyl-2-naphthols can be prepared by the multi-component condensation of aryl aldehydes with 2-naphthol and acetamide or thioacetamide in the presence of an appropriate catalyst such as $RuCl_2(PPh_3)_3$ [6], sulfamic acid [7,8], $Ce(SO_4)_2$ [9], [FemSILP]-L-prolinate [10], $Bi(NO_3)_3{\cdot}5H_2O$ [11], $K_5CoW_{12}O_{40}{\cdot}3H_2O$ [12], $Hf(NPf_2)_4$ [13], $H_3PW_{12}O_{40}$ [14], $Yb(OTf)_3$ [15], $Fe(HSO_4)_3$ [16], montmorillonite K10 clay [17], p-TSA [18], $H_4SiW_{12}O_{40}$ [19], zeolite [20], 2,4,6-trichloro-1,3,5-trizine [21], iodine [22], PFPAT [23], and poly(4-vinylpyridinium butane sulfonic acid) hydrogen sulfate [24].

In most cases, however, the application of these methods is limited by their requirement for prolonged reaction time, ul-

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trasonic or microwave irradiation, and the use of stoichiometric quantities of toxic and corrosive catalysts. Furthermore, the existing procedures generally provide low yields of the desired products. Therefore, the discovery of a new, inexpensive, and readily available catalyst with high catalytic activity and short reaction time for the preparation of amidoalkyl naphthols is strongly desired. Tribromo-melamine (melamine-Br_3) is a homogeneous and non-hygroscopic solid catalyst that can be readily prepared by reaction of melamine with Br under alkali conditions (Scheme 1) [25].

Melamine-Br_3 is stable under a variety of different reaction conditions, including acidic and basic conditions. It is noteworthy that melamine-Br_3 is produced via a facile and clean process that does not require a complicated work-up procedure. Melamine-Br_3 has been used in a variety of different reactions, including the synthesis of 2-aryl thiazolines [25] and the trimethyl silylation of hydroxyl groups with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) [26]. Herein, we report a melamine-Br_3-catalyzed one-pot MCR for the synthesis of biologically interesting 1-amidoalkyl-2-naphthols.

2. Experimental

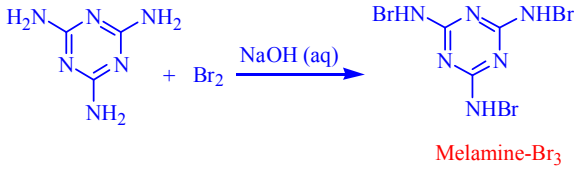
2.1. General procedure for the synthesis of 1-amidoalkyl-2-naphthols

All of the chemicals used here were purchased from Fluka, Merck, and Aldrich chemical companies. The products were characterized by comparison of their spectral (^{1}H and ^{13}C NMR) and physical data with those of authentic samples.

Melamine-Br_3 (0.054 g, 0.15 mmol) was added to a mixture of aldehyde (1 mmol), 2-naphthol (1 mmol) and acetamide or thioacetamide (1.5 mmol), and the resulting mixture was stirred at 130 °C in an oil bath for the appropriate time. Upon completion of the reaction, as determined by TLC, the mixture was cooled to room temperature, and purified directly by column chromatography over silica gel using a mixture of acetone/*n*-hexane (3:7, v/v) as the eluent to give the desired product.

2.2. Condensation of 2-naphthol with terephthaldehyde and acetamide to bis-1-amidoalkyl-2-naphthol

A mixture of terephthaldehyde (0.134 g, 1 mmol), 2-naphthol (0.36 g, 2.5 mmol), acetamide (0.22 g, 3.75 mmol), and melamine-Br_3 (0.054 g, 0.15 mmol) was stirred at 130 °C for the appropriate time. Upon completion of the reaction, as determined by TLC, the mixture was cooled to room temperature and purified directly by column chromatography over silica gel using a mixture of acetone/*n*-hexane (1:1, v/v) as the eluent to give the desired product as a X solid.



Scheme 1. Preparation of melamine-Br_3.

2.3. Spectral data for products

N-((2-Hydroxynaphthalen-1-yl)-(phenyl)methyl))acetamide (**a**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.98 (s, 3H), 7.12–7.38 (m, 6H), 7.76–7.84 (m, 3H), 8.45 (d, J = 8, 1H), 10.0 (s, 1H).

N-((4-Chloro-phenyl)-(2-hydroxynapthalen-1-yl)methyl)acetamide (**b**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.0 (s, 3H), 7.10 (d, J = 8.0 Hz, 1H), 7.17 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.8 Hz, 1H), 7.26–7.33 (m, 3H), 7.39 (m, 1H), 7.78–7.83 (m, 3H), 8.48 (d, J = 8.0 Hz, 1H), 10.06 (s, 1H).

N-((4-Bromo-phenyl)-(2-hydroxynapthalen-1-yl)methyl) acetamide (**c**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.0 (s, 3H), 7.10 (m, 3H), 7.23–7.30 (m, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.80 (m, 3H), 8.49 (d, J = 8.0 Hz, 1H), 10.07 (s, 1H); ^{1}H NMR (400 MHz, DMSO-d_6 + D_2O): δ = 1.98 (s, 3H), 7.07 (m, 3H), 7.20(d, J = 8.8, 1H), 7.26 (m, 1H), 7.38 (m, 3H), 7.77 (m, 3H).

N-((4-Flouro-phenyl)-(2-hydroxynapthalen-1-yl)methyl) acetamide (**d**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.0 (s, 3H), 7.06–7.12 (m, 3H), 7.17–7.3 (m, 4H), 7.39 (m, 1H), 7.77–7.83 (m, 3H), 8.49 (d, J = 8.4, 1H), 10.05 (s, 1H).

N-((2-Hydroxynaphthalen-1-yl)-(2-nitrophenyl)methyl)) acetamide (**e**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.75 (s, 1H), 8.60 (d, J = 8 Hz, 1H), 7.66–7.87 (m, 4H), 7.02–7.48 (m, 6H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 169.0, 153.6, 148.5, 136.8, 133.0, 131.9, 129.8, 128.8, 128.3, 127.9, 127.3, 126.5, 123.8, 122.4, 122.3, 118.3, 116.0, 45.5, 22.1.

N-((3-Nitro-phenyl)-(2-hydroxynapthalen-1-yl)methyl) acetamide (**f**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.04 (s, 3H), 7.27 (m, 3H), 7.43 (t, J = 7.2 Hz, 1H), 7.57 (m, 2H), 7.86 (m, 3H), 8.03 (s, 1H) 8.06 (m, 1H), 8.65 (d, J = 8.0 Hz, 1H), 10.17 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23, 48.1, 118.3, 118.9, 120.9, 121.7, 123.1, 123.3, 127.3, 128.9, 129.2, 130.1, 130.4, 132.6, 133.3, 145.9, 148.2, 153.8, 170.2.

N-((2-Hydroxynaphthalen-1-yl)-(3-hydroxyphenyl)methyl)) acetamide (**g**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.97 (s, 3H), 7.01–7.36 (m, 6H), 7.75–7.81 (m, 4H), 8.39 (d, J = 8.0 Hz, 1H), 9.19 (s, 1H), 9.96 (s, 1H).

N-((2-Hydroxynaphthalen-1-yl)-(4-hydroxyphenyl)methyl)) acetamide (**h**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.96 (s, 3H), 7.0–7.45 (m, 6H), 7.78–7.83 (m, 2H), 8.49 (d, J = 8.0 Hz, 1H), 9.19 (s, 1H), 10.11 (s, 1H).

N-((2-Hydroxynaphthalen-1-yl)-(4-ethoxyphenyl)methyl)) acetamide (**i**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.98 (s, 1H), 8.42 (d, J = 8.0 Hz, 1H), 7.74–7.81 (m, 2H), 6.78–7.37 (m,6H), 3.94 (q, 2H), 1.96 (s, 3H), 1.28 (t, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 169.0, 156.8, 153.0, 134.2, 132.2, 129.0, 128.4, 128.4, 127.1, 126.1, 123.3, 122.3, 118.9, 118.4, 113.8, 62.8, 47.3, 22.6, 14.6.

N-((4-Methyl-phenyl)-(2-hydroxynaphtalen-1-yl)methyl) acetamide (**j**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.99 (s, 3H), 2.24 (s, 3H), 7.1 (s, 1H), 7.23 (d, 1H), 7.24 (d, 4H), 7.26 (m, 1H), 7.75 (m, 1H), 7.78 (d, 1H), 7.79 (d, 1H), 7.82 (d, 1H), 8.44 (s,1H), 9.98 (s,1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 47.61, 118.46, 118.98, 122.32, 125.97, 126.21, 129.1, 128.51, 132.3, 134.9,