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TEA POWDER WASTE: AS A GREEN CATALYST FOR THE SYNTHESIS OF 1-AMIDOALKYL 2-NAPHTHOLS

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Abstract: Tea powder waste is used an efficient natural green catalyst for the one pot three component synthesis of amidoalkyl naphthol using aromatic aldehyde, 2-naphthol and acetamide at reflux condition. The catalyst could be recovered and reused at least five times without appreciable decreasing the catalytic activity. The nontoxic solvent, excellent yield, short reaction time, green synthesis and natural eco-friendly catalyst are the advantages of present protocol.

Keywords: Amidoalkyl naphthol, green synthesis, natural catalyst.

Introduction

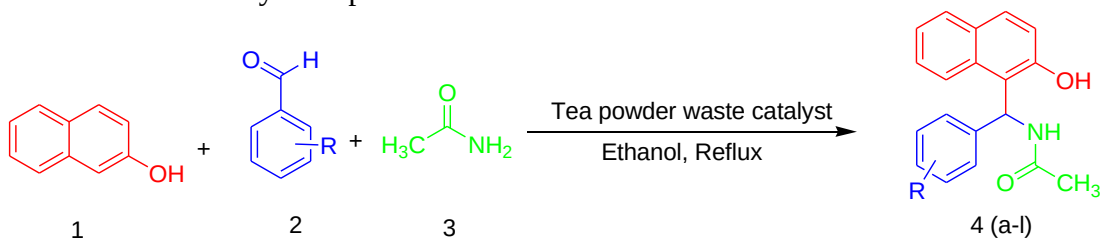
In organic synthesis multi-component reaction are used due to its selectivity and high atom economy. In Ritter type reaction the formation of C-N gives N-alkyl amide compounds are of biologically active ingredients[i]. This type of reaction is associated with condensation of aryl aldehydes, beta naphthol and acetamide in presence of different catalysts like silica sulphuric acid[ii], $Ce(SO_4)_2$[iii], $HClO_4$-SiO_2[iv], $FeCl_3$-SiO_2[v], montmorillonite K10[vi], Ag nanoparticles[vii], bismuth (III) nitrate pentahydrate[viii], nano sulphated zirconia[ix], nano-graphene oxide[x], magnetic nano-Fe_3O_4@SiO_2@Hexamethylene tetramine supported ionic liquid[xi], tetrachlorosilane[xii], $K_5CoW_{12}O_{40}\cdot 3H_2O$[xiii] and cation-exchanged resins[xiv]. The reported methods have some limitations such as use of toxic reagents, tedious work up, hazardous solvent, high reaction temperature and formation of by-products. Therefore, it become a challenge to develop new cost-effective method for synthesis of 1-amidoalkyl-2-naphthols.

According to Research Department of India the consumption of tea powder in India was approximately 1.1 billion kilograms during the financial year 2021. So, the large amount of waste tea powder was introduced in the environment. The tea powder consists of carboxylate, aromatic, phenolic, hydroxyl groups, oxyl groups, carbon and calcium[xv]. The tea waste was used as adsorbent for the removal of dyes and heavy metals[xv]. The attempt was

made in which tea powder waste was used as a heterogeneous catalyst in multi component reactions. In continuation of our research work[xvi-xviii], here we report new cost effective naturally occurring catalyst for the synthesis of 1-amidoalkyl-2-naphthols.

Results and discussion

The reaction was carried out by mixing benzaldehyde (1 mmol), 2-naphthol (1 mmol) and acetamide (1.2 mmol) in presence of 30 mg of tea waste catalyst. The mixture was refluxed with different solvents. The model reaction between benzaldehyde, 2-naphthol and acetamide in presence of tea waste catalyst was used to study the effect of solvent on synthesis of 1-amidoalkyl 2-naphthol derivatives (Table 1). The ethanol was the suitable solvent for the synthesis of 1-amidoalkyl 2-naphthol derivatives.



Scheme 1: Synthesis of 1-amidoalkyl 2-naphthols.

Table: 1 Effect of solvent on synthesis of 1-amidoalkyl 2-naphthols

Sr. No.	Solvent	Time (min)	Yield (%)
1	Solvent free	14	32
2	Water	13	61
3	Methanol	10	64
4	Ethanol	8	92
5	Chloroform	11	51
6	Dimethyl sulfoxide	10	49

The model reaction between benzaldehyde, 2-naphthol and acetamide was refluxed in presence of ethanol and tea waste catalyst to study the effect of amount of catalyst on synthesis of 1-amidoalkyl 2-naphthol derivatives (Table 2). The amount of tea waste catalyst was varied from 10-70 mg, the result shows that the 30 mg of catalyst was sufficient to carry out the reaction.

Table: 2 Effect of amount of catalyst on synthesis of 1-amidoalkyl 2-naphthols

Sr. No.	Amount of catalyst (mg)	Time (min)	Yields (%)
1	10	13	67
2	20	10	78
3	30	8	92
4	40	8	92
5	50	8	92
6	60	8	92
7	70	8	92

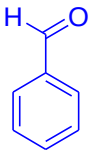
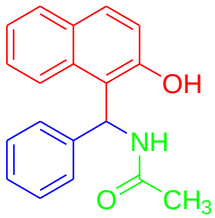
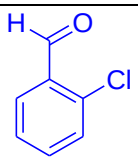
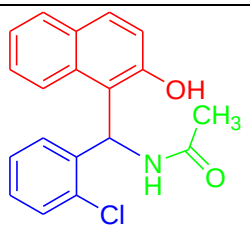
In order to study the effect of time on the synthesis of 1-amidoalkyl 2-naphthols, the model reaction between benzaldehyde, 2-naphthol and acetamide in presence of 30 mg of tea waste catalyst was carried out in the range 2-14 minutes (Table 3). The 8 minutes was the optimum time for the synthesis of 1-amidoalkyl 2-naphthol derivatives.

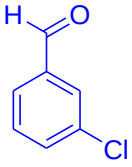
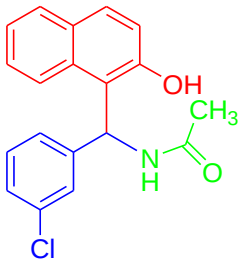
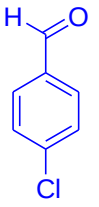
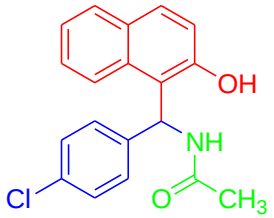
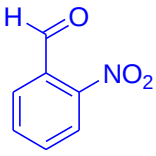
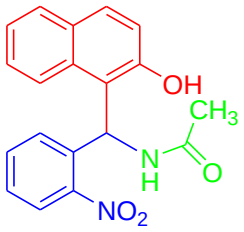
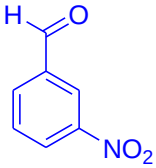
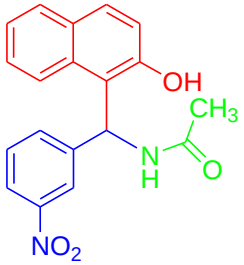
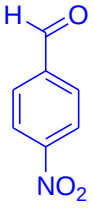
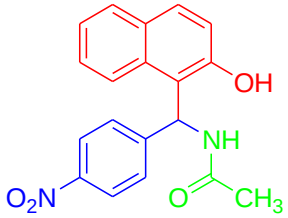
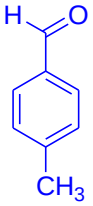
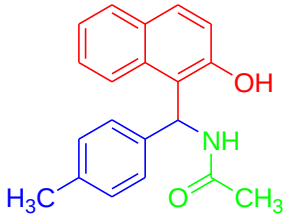
Table: 3 Effect of time on synthesis of 1-amidoalkyl 2-naphthols

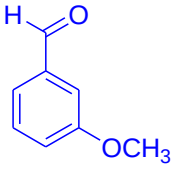
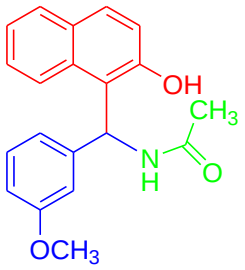
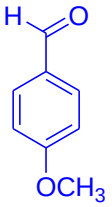
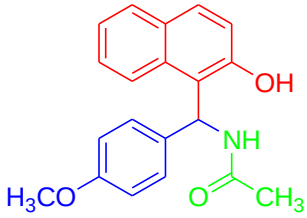
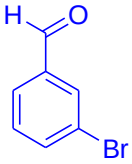
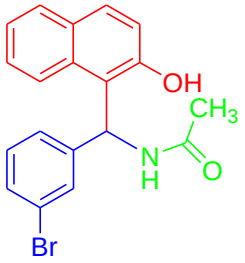
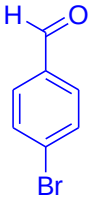
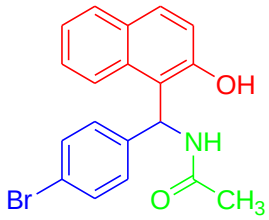
Sr. No.	Time (min)	Yields (%)
1	2	46
2	4	69
3	6	73
4	8	92
5	10	92
6	12	92
7	14	92

In order to check the applicability of the tea waste catalyst, the series of the 1-amidoalkyl 2-naphthol derivatives was synthesized (Table 4). A variety of aromatic aldehydes with electron donating and electron withdrawing groups were converted to 1 amidoalkyl 2-naphthols in excellent yields (88-95 %) with short reaction time (6-18 min). In the present method the 1-amidoalkyl 2-naphthols were the sole products and no by-product was observed.

Table: 4 Synthesis of 1-amidoalkyl 2-naphthol derivatives

Sr. No.	Aldehyde	Product	Time (min)	Yields (%)	M. P (°C)
1		 **4a**	8	92	237-239
2		 **4b**	12	94	191-194

3		 **4c**	14	91	236-238
4		 **4d**	6	90	224-226
5		 **4e**	13	91	215-217
6		 **4f**	7	94	239-241
7		 **4g**	6	95	234-236
8		 **4h**	7	91	218-220

9		 **4i**	16	89	202-204
10		 **4j**	13	90	180-182
11		 **4k**	16	88	227-229
12		 **4l**	18	90	226-228

Experimental

The commercially available chemicals were used without purification. The open capillary method was used to note the melting points. The 1-amidoalkyl 2-naphthol derivatives were matched with known compounds using their spectral data. The Perkin-Elmer FT-IR spectrometer was used to record the IR spectra. The Bruker Avance II (300 MHz) was used to record ^{1}H NMR spectra. The Varian-Saturn GC/MS instrument was used to record mass spectrum of 1-amidoalkyl 2-naphthol derivatives.

Preparation of catalyst

The tea waste was collected, washed with doubled distilled water and dried at room temperature. The waste material was heated in heating oven at 110^{o}C for 3 hrs, for the removal of adsorbed substance and water molecules. The tea waste was then grinded by using mortar and pestle. The tea waste was used again as catalyst in organic reactions.

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

A mixture of aromatic aldehydes (1 mmol), 2-naphthol (1 mmol), acetamide (1 mmol) and tea waste catalyst (0.030 g) were refluxed in presence of ethyl alcohol in oil bath. The

progress of the reaction was monitored by thin layer chromatoghy technique. The solid products obtained were filtered, dried at room temperature.

Compound 4a: ^{1}H-NMR (300 MHz, DMSO-d_6): δ (ppm) 1.95 (s, 3H), 7.11-7.32 (m, 9H),7.75-7.84 (m, 3H), 8.36 (d, *J = 9 Hz*, 1H), 9.92 (s, 1H), ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 23.2, 41.1, 118.4, 120.4, 122.2, 123.7, 124.8, 125.5, 127.4, 128.3, 128.1, 128.2, 128.4, 134.1, 144.2, 152.4, 169.4, MS: m/z 231M^+.

Compound 4f: ^{1}H-NMR (300 MHz, DMSO-d_6): δ (ppm) 2.04 (s, 3H), 7.12-7.45 (m, 6H), 7.74-8.01 (m, 5H), 8.52 (d, *J = 8.1 Hz*, 1H), 10.10 (s, 1H), ^{13}C NMR (75 MHz, DMSO-d_6): 25.51, 66.11, 108.60, 118.12, 120.24, 122.30, 123.92, 125.53, 127.41, 128.10, 129.18, 129.44, 130.81, 132.06, 134.80, 147.67, 148.01, 152.45, 191.65, MS: m/z 276 M^+.

Conclusion

We report here a green protocol for the synthesis of 1-amidoalkyl 2-naphthol derivatives by the condensation of aromatic aldehydes, 2-naphthol and acetamide in presence of naturally available tea waste as a catalyst. The non-toxic solvent, easy work up, high yield and cost effective are the advantages of present method.

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References

i. M. J. Climent, A. Corma and S. Iborra, RSC Adv., 2, 16 (2012).
ii. G. Srihari, M. Nagaraju and M. M. Murthy, Helv. Chim. Acta., 90, 1497 (2007).
iii. N. P. Selvam and T. P. Perumal, Tetrahedron Lett., 47, 7481 (2006).
iv. G. H. Mahdavinia, M. A. Bigdeli and M. M. Heravi, Chin. Chem. Lett., 19, 1171 (2008).
v. H. R. Shaterian and H. Yarahmadi, Tetrahedron Lett., 49, 1297 (2008).
vi. S. Kantevari, S. V. N. Vuppalapati and L. Nagarapu, Catal. Commun., 8, 1857 (2008).
vii. F. Hakimi, Synth. React. Inorg. Met. Org. Chem., 47, 994 (2017).
viii. M. Wang, Y. Liang, T. Zhang and J. Gao, Chin. Chem. Lett., 23, 65 (2012).
ix. A. Zali and A. Shokrolahi, Chin. Chem. Lett., 23, 269 (2012).
x. F Hakimi, F Mirjalili and M Fallah-Mehrjardi, Asian J. Green Chemistry, 4, 183 (2020).
xi. S. Bahrami, S. Jamehbozorgi, S. Moradi and S. Ebrahimi, J Chin. Chem. Soc., 1 (2019).
xii. S. B. Said, M. M. A. Mashaly, A. M. Sheta and S. S. Elmorsy, Int. J. Organic Chemistry, 5, 191 (2015).
xiii. L. Nagarapu, M. Baseeruddin, S. Apuri and S. Kantevari, Catal. Commun., 8, 1729 (2007).
xiv. S. B. Patil, P. R. Singh, M. P. Surpur and S. D. Samant, Syn. Commun., 37, 1659 (2007).
xv. S. Hussain, K. P. Anjali, S. T. Hassan and P. B. Dwivedi, Applied Water Science, 8, 165 (2018).
xvi. A. G. Gadhave, V. A. Kadnor, G. D. Shirole and B. K. Uphade, Heterocyclic Lett., 11, 87 (2021).

xvii. A. G. Gadhave, V. A. Kadnor, B. U. Patil and B. K. Uphade, Heterocyclic Lett., 10, 595 (2020).
xviii. D. S. Aute, A. S. Kshirsagar, B. K. Uphade and A. G. Gadhave, J. Heterocyclic Chem., 57, 3691 (2020).

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