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SHORT COMMUNICATION

TETRAMETHYLAMMONIUM HYDROXIDE (TMAH) AS AN EFFICIENT CATALYST FOR THE ONE-POT SYNTHESIS OF 1,2-DIHYDRO-1-ARYL-NAPHTHO[1,2-e][1,3]OXAZINE-3-ONES UNDER SOLVENT-FREE CONDITIONS

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ABSTRACT. 1,2-Dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-one derivatives were synthesized in high yields using an efficient and one-pot condensation of 2-naphthol, aromatic aldehydes and urea catalyzed by tetramethylammonium hydroxide (TMAH) under solvent-free conditions.

KEY WORDS: TMAH, Naphthoxazine-3-one, Solvent-free reaction, 2-Naphthol, Multi-component reactions

INTRODUCTION

Multi-component reactions (MCRs) have emerged as an efficient and powerful tool in modern synthetic organic chemistry. MCRs allow to chemists for creation of several new bonds in a one-pot reaction. Strecker was the first chemist that used MCRs for the synthesis of amino acids [1]. In the past decade, there have occurred tremendous developments in MCRs and great efforts are continually being made to develop new MCRs [2-6].

Oxazinone derivatives are an important class of heterocyclic compounds because their biological activities [7]. For example, Latif and his co-workers synthesized 3,4-dihydro-2H-1,3-oxazin-2-ones by intramolecular cyclization of (2-nitroetheny1)aryl N-arylcarbamates and investigated their antimicrobial activities [8]. Also, Wang used this class of compounds as precursors in the preparation of chiral amino phosphine ligands for application in asymmetric catalysis [9]. However, to the best of our knowledge, only few reports exist on the synthesis of naphthalene-condensed oxazinone derivatives in the literature [8-11]. Recently, some derivatives of naphthalene-condensed 1,3-oxazin-3-ones were synthesized using condensation of amino alkylnaphthols in the presence of triethylamine [12]. A new method for the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-ones is the reaction between 2-naphthol, aromatic aldehydes and urea, but this reaction need to catalyst for promotion. Mahdavinia and his co-workers prepared these compounds in the presence of $HClO_4$-SiO_2 [13]. Also Bazgir and his co-workers accomplished this reaction by use of MW irradiation [14]. Although these methods provide an improvement, in most cases long reaction times, low selectivity, forceful conditions, or tedious work-up are needed. In addition, some of the reagents are expensive and toxic. Therefore, the development of new, efficient and green methods for the synthesis of naphthoxazinone derivatives is in demand.

In continuation of our pervious works on the applications of catalysts in the synthesis of heterocyclic compounds[15, 16], in this article, we present a one-pot, three-component method for the preparation of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-one derivatives in the presence of tetramethylammonium hydroxide (TMAH) at room temperature under solvent-free conditions (Scheme 1).

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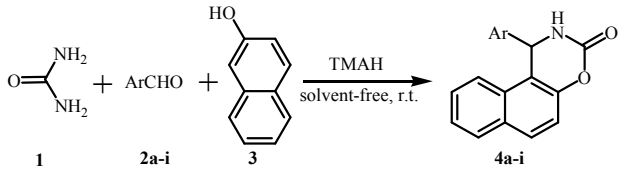


Scheme 1. TMAH catalyzed synthesis of 1,2-dihydro-1-aryl-naphtho[1,2-e][1,3]oxazine-3-ones.

RESULTS AND DISCUSSION

To optimize the reaction conditions, we carried out the reaction of benzaldehyde (1 mmol), urea (2 mmol) and 2-naphthol (1 mmol) under solvent-free conditions at room temperature, but did not obtain any product (Table 1, entry 1). Then, we used different amounts of TMAH as catalyst and the best result was obtained using 35 mol% of catalyst (Table 1, entry 5).

Table 1.Effect of TMAH amount on the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-ones[a].

Entry	Mol% of cat.	Time (min)	Yield (%)[b]
1	—	180	Trace
2	10	160	87
3	20	160	91
4	30	140	94
5	35	120	98
6	40	120	95

[a]1 mmol 2-naphthol, 1 mmol benzaldehyde, and 2 mmol urea undersolvent-free conditions at room temperature.
[b]Isolated yields based on 2-naphthol.

For investigation of solvent effect in this reaction, different solvents were used. As shown in Table 2 both type of solvents, protic and aprotic, lead to decreasing of the reaction yield and the best yield can be obtained in the solvent-free conditions.

Table 2. Effect of solvent on the reaction conditions[a].

Entry	Solvent	Time (min)	Yield (%)[b]
1	H_2O	180	68
2	EtOH (96%)	240	33
3	EtOH (70%)	240	37
4	MeOH	150	46
5	$CHCl_3$	180	40
6	CH_3CN	150	72
7	—	120	98

[a]1 mmol 2-naphthol, 1 mmol benzaldehyde, 2 mmol urea and 35 mol% TMAH at room temperature.
[b]Isolated yields based on 2-naphthol.

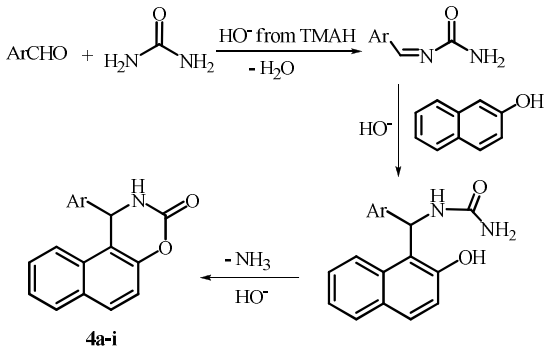
After optimization of the reaction conditions to examine the generality of the process, several experimental trials illustrating this method for the synthesis of derivatives were conducted. The results are summarized in Table 3. Benzaldehyde and other aromatic aldehydes containing electron-withdrawing groups (halide and nitro groups) or electron-donating groups (such as hydroxy, alkoxyl and methyl groups) were employed which were found to react well to give the corresponding 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-ones in good yields.

Table 3. TMAH catalyzed synthesis of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-ones **4a-g**[a].

Entry	Product[b]	Ar	Yield (%)[c]	m.p. (°C) [Ref.]
1	**4a**	4-ClC_6H_4	97	218-220 [13]
2	**4b**	4-$MeOC_6H_4$	98	184-186 [13]
3	**4c**	C_6H_5	98	220-221 [14]
4	**4d**	3-$NO_2C_6H_4$	95	226-228 [13]
5	**4e**	4-$NO_2C_6H_4$	90	186-189 [11]
6	**4f**	3-BrC_6H_4	92	229-231 [13]
7	**4g**	4-HOC_6H_4	90	182-184 [13]
8	**4h**	2-ClC_6H_4	94	253 [13]
9	**4i**	4-MeC_6H_4	89	166-168 [14]

[a]Reaction conditions: 2-naphthol 1 mmol, benzaldehyde 1 mmol, urea 2 mmol, and TMAH 35 mol% at room temperature under solvent-free conditions. [b]All products were characterized by use of IR, and ^{1}H NMR spectral data, and comparison of their melting points with those of authentic samples. [c]Isolated yields based on 2-naphthol.

The catalyst plays a crucial role in the success of the reaction in terms of the rate and the yield. The possible mechanism for the synthesis of products **4a-i** in the presence of TMAH as a promoter is shown in Scheme 2. On the basis of this mechanism, TMAH catalyzes the reaction by increasing the nucleophilic character of the necleophiles, urea and 2-naphthol, in the reaction. Successive elimination of NH_3 results in the formation of the products [14].



Scheme 2. Proposed mechanism.

EXPERIMENTAL

Chemicals were purchased from Merck and were used without further purification. All yields refer to the isolated products. The purity determination of the substrate and reaction monitoring were accompanied by thin layer chromatography (TLC) on silica-gel polygram SILG-UV 254 plates.

Typical procedure. A mixture of an aromatic aldehyde (1 mmol) and urea (2 mmol) stirred in the presence of TMAH (35 mol %) for 20 min, then 2-naphtol (1 mmol) was added to the mixture and the reaction continually stirred for 2 hours. After the completion of the reaction (monitored by TLC), the reaction mixture was washed with ethylacetate (5 mL). The solid product was obtained by recrystalization from ethanol. Products were characterized by their

physical constants (m.p.), IR and ^{1}H NMR spectroscopy and comparison with authentic samples.

Representative IR and ^{1}H NMR spectral data for the selected products. 1,2-Dihydro-1-(4-chlorophenyl)naphtho[1,2-][1,3]oxazine-3-one **(4a)**: m.p. = 218–220 ^{o}C; IR (KBr): 3224, 3146, 1734 cm–1; ^{1}H NMR (300 MHz, DMSO- d_6): δ = 5.83 (s, 1 H, CH), 6.9–7.6 (m, 10 H, Ar–H), 8.49 (s, 1 H, NH). 1,2-Dihydro-1-(2-chlorophenyl)naphtho[1,2-e][1,3] oxazine-3-one **(4h)**: m.p. = 253 ^{o}C; IR(KBr): 3237, 3124, 1727 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.50 (d, 1H, J = 2.94, CH), 7.18-8.01 (m, 10H, Ar-H), 8.89 (s, 1H, NH).

CONCLUSION

In conclusion, we have described a highly efficient one-pot synthesis for the preparation of naphthoxazine-3-one derivatives in three-component cyclocondensation reaction of 2-naphtol, aromatic aldehydes and urea under solvent-free conditions. Easy work-up, low cost, ready commercial availability of the catalyst make the procedure an attractive alternative to the existing methods for the synthesis of naphthoxazine-3-one derivatives.

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