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Synthesis of 1,2,3,4-Tetrahydroquinolines Using $AlCl_3$ in Aqua Mediated

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ABSTRACT. Catalytic performance of Lewis acids have been investigated in the synthesis of 1,2,3,4-tetrahydroquinolines via cyclocondensation reaction of aniline derivatives with cyclic enol ethers such as 3,4-dihydro-2*H*-pyran and 2,3-dihydrofuran. The catalytic activity of various of these catalysts in different solvents was compared with other classical catalysts such as KSF clay (1.5 g), $InCl_3$ (10–20 mol%), $ZrOCl_2$ (10 mol%), $Sc(OTf)_3$ (3 mol%), PANI–$InCl_3$ (10 mol%), I_2 (20 mol%), $InCl_3$ (5 mol%), 4-npa (25 mol%) and Cellulose–SO_3H (0.03 g).

Key words: Catalytic, Pyran, Furan, Tetrahydroquinoline, Synthesis

INTRODUCTION

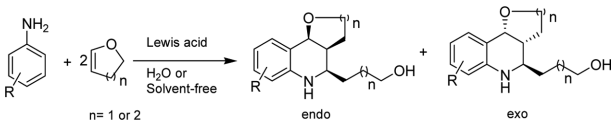
Tetrahydroquinoline derivatives exist in the variety of natural products and pharmaceutical agents that show broad biological activities.[1] Several synthetic procedures for the preparation of tetrahydroquinoline derivatives have been reported.[2] Also three-component-reaction of a substituted aniline, an aryl aldehyde, and an electron-rich olefin using Lewis acid has also been reported.[3] Recently, tetrahydroquinolines have been synthesized via a diamino coupling of aniline derivatives and cyclic enol ethers catalyzed by $InCl_3$ in water[4] or CH_3CN,[5] KSF clay,[6] $Sc(OTf)_3$ in $[Bmim]PF_6$,[7] iodine molecular,[8] $ZrOCl_2$,[9] PANI–$InCl_3$,[10] 4-npa,[11] Cellulose–SO_3H[12] and $FeCl_3$–NaI and TMSCl–NaI by aryl azids[13,14] have also been reported. However, a number of modified methods under improved conditions have been reported, many of them suffer from drawbacks such as utilizing of stiochemetric amounts of reagents including $FeCl_3$–NaI (1.5:1, reagent:substrate), iodine (20 mol%) in CH_2Cl_2, $InCl_3$ (5 mol%), KSF clay (1.5 g) and TMSCl–NaI (1.5:1, reagent: substrate). Owing to their significant biological activity, there is still a need for a simple, green and general procedure for the one-pot synthesis of tetrahydroquinolines under catalytic conditions.

On the other hand, Lewis acids accelerate a wide range of organic reactions by binding to and thereby activating reactants. This activation often results in rate increases of many orders of magnitude compared with the thermal reaction.

Lately, $AlCl_3$ has been employed for the synthesis of 5-benzoylacenaphthene,[15] selective synthesis of 2-aryl-2*H*- and 4-aryl-4*H*-3,5-diformylpyrans from acetal with aromatic aldehydes,[16] catalytic asymmetric arylation of aldehydes,[17] catalytic beckmann rearrangement of ketoximes,[18] conversion of isopropenyl acetate into 3-acetyl- and 3,5-diacetyl-2,6-dimethyl-4*H*-pyran-4-ones,[19] one-pot four-component synthesis of 1,4-dihydropyridines and their aromatization,[20] hydrosilylation of alkynes with hydropolysilanes,[21] cycloadditions of activated cyclopropanes and aromatic aldehydes,[22] synthetic routes to sterically hindered unsymmetrical diaryl ketones via arylstannanes,[23] one-pot preparation of 1,1,3-triheteroaryl compounds of crotonaldehyde and indole,[24] 1-substituted 1,2,3,4-tetrahydrobenz[*g*]isoquinoline-5,10-diones,[25] synthesis of 5-amino-4-arylazo-3-methyl-1*H*-pyrazoles and 5-aryl-3-methylpyrazole[3,4-e] [1,2,3,4] tetrazines[26] and oxidation of alcohol.[27]

The replacement of environmental hazardous catalysts in various processes, with green catalysts, solvent-free and on water reaction is of the innovative trends. In recent years, with the increase of environmental consciousness in chemical research and industry, efficient, economic and clean procedures have received increased attention. Thus, water has become an intriguing reaction medium, and has particularly captured the interest of organic chemists.[30–33] Reactions previously thought impossible in water are now a reality. In many cases the catalyst and/or the aqueous medium can be recovered and reused, thereby reducing the environment impact of the reaction process.[34] Many Lewis acids also work well in aqueous medium,[35] and even $AlCl_3$, $SnCl_2$ and $TiCl_4$ which are previously used under anhydrous conditions are excellent catalysts in water.[31]

Ongoing previously our research to introduce the green protocol for the synthesis of heterocyclic compounds using eco-friendly catalysts,[28,29] we interest to report catalytic synthesis of pyrano-and furano-quinoline derivatives using



***Scheme* 1.** Synthesis of pyrano- and furano [3,2-*c*]quinolines.

aryl amines, 3,4-dihydro-2*H*-pyran (DHP) and 2,3-dihydrofuran (DHF) in water or solvent-free and in the presence of Lewis acids as catalyst under mild condition (*Scheme* 1).

RESULTS AND DISCUSSION

In this study, the effect of various parameters such as catalyst type, solvent type, temperature, and reaction time on the yield of products were studied and compared with those obtained using other reagents. That also found $AlCl_3$ catalyst in water as a solvent is an eco-friendly catalyst for aforementioned cyclocondensation reaction.

Effect of the Solvent

The cyclocondensation reaction of 4-methoxyaniline with cyclic enol ethers, such as 3,4-dihydro-2*H*-pyran was carried out in various solvents, such as water, acetonitrile, ethanol, dimethylsulfoxide, toluene, carbon tetrachloride and under solvent-free condition. We found that water is the most effective solvent (*Table* 1). It is noteworthy to mention that heating of the reactants in neat water without any catalyst did not give the products even in prolonged reaction time.

Effect of the Catalyst Type

Comparison of $AlCl_3$, $Al(NO_3)_3.9H_2O$, $Al(DS)_3.3H_2O$, Al_2O_3, $AlO_3C_9H_{21}$ showed that the higher activity could be achieved with $AlCl_3$ (*Table* 2). Although it is difficult to offer an explanation for the different activity between these Lewis acids, certainly there is a relationship between the cation activity and structure of anion. By changing the constituent anion the acid strength of Al^{3+} as well as its catalytic activity is able to vary in a wide range.

***Table* 2.** Synthesis of 1,2,3,4-tetrahydroquinolines using different Al^{3+}salts (15 mol%)[a]

Entry	Catalyst	Solvent (5 ml)	Time (h)	Yield (%)[b]	*endo/exo*[c]
1	$AlCl_3$	H_2O	2.5	92	65:35
2	$AlCl_3$	free	30	Trace	–
3	$Al(NO_3)_3.9H_2O$	H_2O	14	85	54:46
4	$Al(NO_3)_3.9H_2O$	free	3	88	54:46
5	$Al(DS)_3.3H_2O$[d]	H_2O	7	12	–
6	$Al(DS)_3.3H_2O$	free	7	10	–
7	Al_2O_3	H_2O	72	Trace	–
8	Al_2O_3	free	30	Trace	–
9	$AlO_3C_9H_{21}$	H_2O	72	Trace	–
10	$AlO_3C_9H_{21}$	free	30	Trace	–

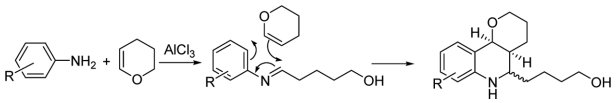
[a]Reaction condition: 4-methoxyaniline (1.0 mmol) and 3,4-dihydro-2*H*-pyran (2.2 mmol) at 50 ºC. [b]Isolated yield. [c]Determined by ^{1}H NMR spectroscopy. [d]Aluminum tris (dodecyl sulfate) trihydrate.

This methodology has been generalized by reaction of series of substituted aryl amines with 3,4-dihydro-2*H*-pyran and 2,3-dihydrofuran to give pyrano-and furano-quinolines as illustrated in Table 3. The results showed that aryl amines bearing electron donating groups are more reactive than those of with electron withdrawing groups. Furthermore by employing 4-nitroaniline, the desired products could be obtained upon reaction with 3,4-dihydro-2*H*-pyran under similar conditions in longer reaction time and less yield (*Table* 3, entry 7). In most cases, the products were obtained as a mixture of endo- and exo-isomers. In all cases the existence of the endo isomer is predominant. The ratio of isomers was determined from the ^{1}H NMR spectra of the products. The stereochemistry of the isomers was assigned

***Table* 1.** Comparison catalytic synthesis of 1,2,3,4-tetrahydroquinolines using $AlCl_3$ and varying solvents.[a]

Entry	Solvent (5 ml)	Catalyst (mol%)	Temp (ºC)	Time (h)	Yield (%)[b]	*endo/exo*[c]
1	free	15	25	72	Trace	–
2	free	15	50	30	Trace	–
3	H_2O	10	50	15	85	65:35
4	H_2O	15	25	48	30	–
5	H_2O	15	50	2.5	92	65:35
6	H_2O	20	50	2.5	92	65:35
7	CH_3CN	15	50	55	Trace	–
8	EtOH	15	50	55	Trace	–
8	DMSO	15	50	12	70	–
10	Toluene	15	50	16	Trace	–
11	CCl_4	15	50	16	Trace	–

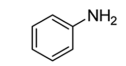
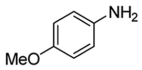
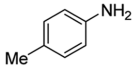
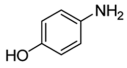
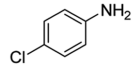
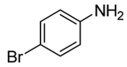
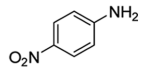
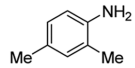
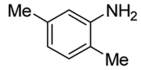
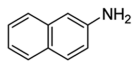
[a]Reaction condition: 4-methoxyaniline (1.0 mmol), 3,4-dihydro-2*H*-pyran (2.2 mmol). [b]Isolated yield. [c]Determined by ^{1}H NMR spectroscopy.



***Scheme* 2.** The proposed reaction mechanism for $AlCl_3$ -catalyzed pyrano quinoline derivative.

on the basis of coupling constants and chemical shifts of protons which was accordant with the presentation of the literature.[13] It is noteworthy that our method has several advantages including mild conditions, good yields, short reaction times and simple operation and work-up. Additionally, the protocol does not require anhydrous solvents adopted the principles of green chemistry point of view.

***Table* 3.** Synthesis of 1,2,3,4-tetrahydropyanoquinolines using $AlCl_3$.[a]

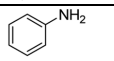
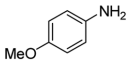
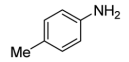
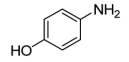
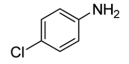
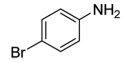
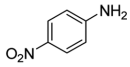
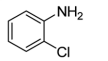
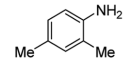
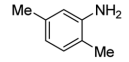
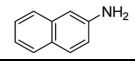
Entry	Aryl amine	Time (h)	Condition	Yield (%)[b]	*endo*/*exo*[c]
1		3	H_2O/50 ºC	88	77:23
2		2.5	H_2O/50 ºC	92	65:35
3		2.5	H_2O/50 ºC	90	70:30
4		2.5	H_2O/50 ºC	85	73:27
5		10	H_2O/50 ºC	82	62:38
6		11	H_2O/50 ºC	80	79:21
7		13	H_2O/50 ºC	55	58:42
8		3	H_2O/50 ºC	88	71:29
9		10.5	H_2O/50 ºC	83	64:36
10		3	H_2O/50 ºC	87	69:31
11		3	H_2O/50 ºC	89	68:32
12		5	H_2O/50 ºC	80	60:40
13		No reaction	H_2O/50 ºC	–	–

[a]Reaction condition: aryl amine (1.0 mmol), DHP (2.2 mmol) and $AlCl_3$ (15 mol%). [b]Isolated yield. [c]Determined by ^1H NMR spectroscopy.

The plausible mechanism of the product formation is shown in *Scheme* 2. Z. Lei and co-worker[27] have previously been reported that $AlCl_3$ is hydrolyzed to oligomers $[Al_2(OH)_nCl_{6-n}]_m$ in aqueous phase, the hydrolyzed products have been regarded as water-soluble supporter the in situ formed Al–OH was possibly applied as key intermediate for alcohol oxidation. On the other hand $AlCl_3$ is a hard Lewis acid that coordinates hard basic centers like the oxygen atom of a carbonyl group and that of enol ether activating the reagent for a nucleophilic attack. Thus either $AlCl_3$ or Al–OH may catalyzed an aza-Diels–Alder process of 2-azadiene which is generated in situ from cyclic enol ether and aniline derivatives using Al^{+3} catalyst, with another equivalent of cyclic enol resulting in the formation of trahydroquinoline.

To show the merits and advantages of using $AlCl_3$ as a catalyst in the synthesis of 4-(9-methoxy-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-c]quinolin-5-yl)butan-1-ol (*Table* 3, entry 2), our protocol was compared with previously reported methods (*Table* 5). From the results reported, the advantages of our method are evident regarding the yields of the reactions which are very important in chemical industry especially when it is combined by green reaction conditions.

***Table* 4.** Synthesis of 1,2,3,4-tetrahydrofuranoquinolines using $AlCl_3$.[a]

Entry	Aryl amine	Time (h)	Condition	Yield (%)[b]	*endo*/*exo*[c]
1		2.5	H_2O/R.T.	88	78:22
2		1.45	H_2O/R.T.	90	75:25
3		1.45	H_2O/R.T.	86	80:20
4		1.45	H_2O/R.T.	83	80:20
5		8	H_2O/50 ºC	79	77:23
6		8	H_2O/50 ºC	82	82:18
7		10	H_2O/50 ºC	59	52:48
8		7	H_2O/50 ºC	81	67:33
9		2	H_2O/R.T.	80	74:26
10		2	H_2O/R.T.	86	66:34
11		5	H_2O/R.T.	82	56:44

[a]Reaction condition: aryl amine (1.0 mmol), DHF (2.2 mmol) and $AlCl_3$ (15 mol%). [b]Isolated yield. [c]Determined by ^1H NMR spectroscopy.

EXPERIMENTAL

Materials and Methods

^{1}H NMR spectra were recorded on a Bruker ARX 300 MHz using $CDCl_3$ and DMSO as the solvent and TMS as an internal standard. IR spectra were recorded on KBr pellets using a FT-IR Bruker Tensor 27 spectrometer. The reactions were monitored by TLC. All solvents and reagents were purchased from Aldrich and Merck with high-grade quality and used without any purification and $Al(DS)_3.3H_2O$ was prepared via previously reported protocol in literature.[36] All products were known and their physical and spectral data were compared with those of authentic samples (lit. [4-14]).

General Procedure for the Synthesis of 1,2,3,4-Tetrahydropyranoquinolines Using $AlCl_3$. A Typical Procedure

A mixture of aniline derivatives (1 mmol), cyclic enol ether (2.2 mmol) and of $AlCl_3$ (15.0 mol%) in water (5.0 ml) was stirred at ambient temperature or at 50 ºC for an appropriate time (*Table* 3,4). The progress of the reaction was monitored by TLC (ethyl acetate:n-hexane 2:3). Upon completion of the reaction, ethylacetate (15×2) was added and the organic layer was separated. After drying of organic phase (Na_2SO_4), and evaporation of the solvent, the crude product was afforded which was directly subjected to thin layer chromatography. The product was as a mixture of endo/exo isomers. The aqueous layer that remained after the work-up of the reaction can be reused.

Physical and Spectra Data for New Products

5-(4-hydroxybutyl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinolin-7-ol (entry 8, Table 3)

IR (KBr, cm^{-1}): 3412.13, 2937.56, 2859.81, 1615.09, 1509.02, 1448.08, 1377.66, 1204.37, 1073.40, 860, 743.04.

endo-isomer ^{1}H NMR (DMSO, 300 MHz): δ 1.25–1.7 (m, 10H), 1.9 (m, 1H, H_6), 3.25 (m, 1H), 3.35–3.42 (m, 2H), 3.54 (t, J = 6.2 Hz, 2H), 4.5 (s, 1H, OH), 4.94 (d, J = 5.46, 1H, H_5), 6.43 (t, J = 7.6, 1H, Ar–H), 6.55 (d, J = 7.5, 1H, Ar–H), 6.67 (d, J = 7.5, 1H, Ar–H).

exo-isomer ^{1}H NMR (DMSO, 300 MHz): δ 1.25–1.7 (m, 10H), 1.8 (m, 1H, H_6), 3.32 (m, 1H), 3.4 (m, 3H), 3.72 (m, 1H), 4.16 (s, 1H, OH), 4.33 (d, J = 2.45, 1H, H_5), 6.32 (t, J = 7.6, 1H, Ar–H), 6.53 (d, J = 7.5, 1H, Ar–H), 7.61 (d, J = 7.5, 1H, Ar–H).

4-(7,9-dimethyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c] quinolin-5-yl)butan-1-ol (entry 11, Table 3)

IR (KBr, cm^{-1}): 3391.28, 2932.78, 2854.42, 1589.90, 1507.42, 1466.06, 1378.23, 1211.64, 1056.65, 861.78, 790.

endo-isomer ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.4–1.8 (m, 10H), 2.1 (m, 1H, H_6), 2.3 (s, 6H), 3.36 (m, 1H), 3.61 (m, 2H), 3.65 (t, J = 6.43, 2H), 5 (d, J = 5.46, 1H, H_5), 6.46 (d, J = 7.4,1H, Ar–H), 6.87 (d, J = 7.4, 1H, Ar–H).

exo-isomer ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.4–1.8 (m, 10H), 1.95 (m, 1H, H_6), 2.2 (s, 6H), 3.51 (m, 1H), 3.73 (m, 3H), 3.99 (m, 1H), 4.4 (d, J = 2.33, 1H, H_5), 6.46 (d, J = 7.4, 1H, Ar–H), 6.87 (d, J = 7.4, 1H, Ar–H).

3-(6-chloro-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinolin-4-yl)propan-1-ol (entry 8, Table 4)

IR (KBr, cm^{-1}): 3426.20, 2941.11, 2848.95, 1598.87, 1510.12, 1464.34, 1375.00, 1205.08, 1077.68, 867.48, 743.17.

endo-isomer ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.72–1.86 (m, 5H), 1.92–2.01 (m, 1H), 2.60 (m, 1H), 3.43 (m, 1H), 3.53 (m, 2H) , 3.65 (m, 2H), 5.08 (d, J = 7.0, 1H), 6.65 (t, J = 7.3, 1H), 7.12 (d, J = 7.8, 1H), 7.17 (d, J = 7.9, 1H).

exo-isomer ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.72–1.86 (m, 5H), 1.92–2.01 (m, 1H), 2.62 (m, 1H), 3.65 (m, 2H), 3.77 (m, 2H), 3.96 (m, 1H), 4.55 (d, J = 5.25, 1H), 6.59 (t, J

***Table* 5.** Comparison synthesis of 4-(9-methoxy-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano [3,2-*c*] quinolin-5-yl)butan-1-ol using varying catalysts

Catalyst	Condition	amine/enolether[a]	Time (h)	Yield (%)[b]	*endo/exo*[c]	Ref.
$InCl_3$ (10–20%)	H_2O, 50 °C	2: (4–6)	10	62	66:34	4
$InCl_3$ (5%)	CH_3CN, r.t	5:12	3.5	87	85:15	5
KSF Clay (1.5 g)	CH_3CN, r.t	5:12	3.5	88	95:5	6
$Sc(OTf)_3$ (3%)	[bmim]PF_6, r.t	2:5	3.5	87	95:5	7
I_2 (20%)	CH_3CN, r.t	1:2	0.8	83	33:67	8
$ZrOCl_2$ (10%)	H_2O, 50 °C	1:3	2	72	68:32	9
PANI-$InCl_3$ (10%)	H_2O, 50 °C	0.5:1.5	5	90	59:41	10
4-npa (25%)	CH_3CN, 50 °C	1:2.5	3.5	86	45:55	11
Cellulose-SO_3H (0.03 g)	CH_3CN, r.t	5:10	4.5	74	79:21	12
$AlCl_3$ (15%)	H_2O, 50 °C	1:2.2	2.5	92	65:35	This work

[a]Aryl amine: 4-methoxyaniline, enolether: DHP. [b]Isolated yield. [c]Determined by ^{1}H NMR spectroscopy.

= 7.3, 1H), 7.12 (d, *J* = 7.8, 1H), 7.20 (d, *J* = 7.9, 1H).

3-(6,8-dimethyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinolin-4-yl)propan-1-ol (entry 10, Table 4)

IR(KBr, cm^{-1}): 3418.59, 2933.96, 2857.92, 1588.07, 1505.30, 1455.47, 1378.91, 1213.52, 1058.02 , 865.678, 794.48.

endo-isomer ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.60–1.92 (m, 5H), 1.98–2.02 (m, 1H), 2.25 (s, 6H), 2.60 (m, 1H), 3.32 (m, 1H), 3.80 (m, 2H), 3.90 (m, 2H), 5.26 (d, *J* = 8.523, 1H), 6.55 (d, *J* = 7.45, 1H), 7.88 (d, *J* = 7.47, 1H).

exo-isomer ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.60–1.92 (m, 5H), 1.98–2.02 (m, 1H), 2.25 (s, 6H), 2.60 (m, 1H), 3.69 (m, 2H), 3.74 (m, 2H), 3.98 (m, 1H), 4.57 (d, *J* = 5.025, 1H), 6.55 (d, *J* = 7.45, 1H), 7.88 (d, *J* = 7.47, 1H).

CONCLUSION

In summary, we reported efficient, simple and green conditions for the synthesis of tetrahydro pyrano and furano quinoline derivatives as endo/exo isomers. The employed catalyst for this process is rather inexpensive, non-stinking, nontoxic hence this is a practical protocol.

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