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One Pot Highly Efficient Synthesis of Furano and Pyranoquinoline Derivatives In Ambient Conditions

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Abstract

Various derivatives of pyranoquinoline were synthesized from aniline, substituted benzaldehyde and dihydrofuran, pyran by using ferric chloride. The catalyst possesses better catalytic activity as 100% conversion of reactant with 80% yield in two hour using 10 wt% of ferric chloride. Finally catalyst was easily separated and recycled without loss of significant catalytic activity from reaction mixture. Derivatives of pyranoquinoline was charecterised by spectroscopic techniques as 1H NMR,C^{13}NMR, Mass etc. The present methodology is proved to be highly efficient, ecofriendly synthesis of furano, pyranoquinoline via Imino Diels-Alder Reactions.

Keywords: Ferric chloride, pyranoquinoline, furanoquinoline, Diels-Alder reaction, efficient synthesis

1. Introduction

Furano, Pyranoquinoline derivatives were received much attention in the field of medicinal chemistry, due to their wide range of biological applications such as antipyretic, anti-inflammatory, antiallergic, analgesic, antiplatelet, psychotropic and estrogenic[1-5]. Imino Diels-Alder reaction is important synthetic route for construction of tricyclic ring containinig nitrogen heterocycle. Various derivatives of pyranoquinoline was prepared from substituted aniline, aldehyde and 2,3 dihydrofuran or 3,4-dihydro-2H-pyran has been reported by using variety of lewis acid catalyst like $SbCl_3$, $InCl_3$[5], $BiCl_3$, $GdCl_3$, $CuCl_2$, $LiClO_4$, SmI_2, $ZrCl_4$, $Bf_3.OEt_2$, and Bronsted acids such as TFA, P-TsOH, $KHSO_4$, $Sb_2(SO_4)_3$[6-11]. Another attempts was done with ionic liquid[6] and also by using phosphomolybdic acid. Recently reported one pot synthesis of pyranoquinoline using tartarateboronic acid catalyst at room temperature with formation of endo and exo isomers in 1:2 ratio.

Heterogeneous catalyst are more important in organic transformation due to ease of handling, easy work up, high yield, high selectivity, reusability comparative to homogeneous catalyst. Green Solvent for organic reactions lead to new synthetic approach and helpful to maintain the atmosphere. These reactions show various advantages over traditional reactions that takes place in organic solvents, such reactions are

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reducing the load of organic solvent disposal and enhance the rate of many organic reactions [18]. Therefore, the development of an environmental benign heterogeneous catalytic system which is more efficient, highly selective, and inexpensive for the synthesis of pyranoquinolines in green solvent is highly desirable. Herein, we wish to report the tandem synthesis of pyranoquinolines by using ferric chloride as a heterogeneous catalyst.

2. Experimental

All the chemicals and reagent required for preparation of catalyst and synthesis of pyranoquinoline are purchased from Sigma Aldrich and SD Fine of research grade. Solvents were purchased from commercial sources and purified by distillation before its use. All the reactions are performed in open air under solvent free condition at room temperature.

Procedure:

Benzaldehyde (1 mmol) and aniline (1mmol) add 3,4-dihydropyran or 2,3-dihydrofuran (1.2 mmol) ,then addition of 10 mol % catalyst in Ethanol-water solvent at reflux condition for appropriate time. The reaction mixture was then quenched with ice and saturated sodium bicarbonate solution. The resultant product was extracted with chloroform, and washed with brine and dried over anhydrous sodium bisulphate then filter it and evaporated the solvent. The residue was again purified by column chromatography by using silica gel and ethyl acetate\ pet ether as eluent to get upto 80 % yield.

4-Phenyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]- quinoline. White solid, mp 93–958C (lit,5b mp 958C); 1H NMR (CDCl3): d 1.55 (m, 1H), 2.25 (m, 1H), 2.75 (m, 1H), 3.80 (m, 3H), 4.70 (d, 1H, J¼2.8 Hz), 5.25 (d, J¼8.0 Hz, 1H), 6.58 (d, J¼8.0 Hz, 1H), 6.80 (t, J¼8.0 Hz, 1H), 7.05 (t, J¼8.0 Hz, 1H), 7.35–7.55 (m, 6H). 13C NMR (CDCl3) d: 24.5, 45.8, 57.3, 66.6, 75.9, 114.9, 119.0, 122.5, 126.3, 127.6, 128.2, 128.6, 130.0, 142.3, 144.8. EIMS: m/z: 251 Mþ, 220, 206, 174, 130, 91. IR (KBr): 3348, 2975, 2855, 1615, 1480, 1070 cm^{-1}. Anal. calcd for $C_{17}H_{17}NO$ (251.32): C, 81.24; H, 6.82; N, 5.57. Found: C, 81.26; H, 6.83; N, 5.58.

8-Methoxy-4-phenyl-2,3,3a,4,5,9b-hexahydro furo[3,2-c]quinoline. Pale yellow solid, mp 132– 1338C (lit,5b mp 132–1338C); 1H NMR (CDCl3): d 1.55 (m, 1H), 2.20 (m, 1H), 2.75 (m, 1H), 3.65–3.85 (m, 3H), 3.78 (s, 3H), 4.62 (d, J¼2.8 Hz, 1H), 5.22 (d, J¼8.0 Hz, 1H), 6.50 (d, J¼8.6 Hz, 1H), 6.74 (dd, J¼8.6, 2.8 Hz, 1H), 6.94 (d, J¼2.8 Hz, 1H), 7.25–7.45 (m, 5H). 13C NMR (CDCl3) d: 24.3, 45.8, 55.7, 57.9, 66.7, 76.3, 113.8, 115.9, 116.3, 123.5, 126.5, 127.4, 128.6, 139.0, 142.5, 153.0. EIMS: m/z: 281 Mþ, 236, 206, 160, 141, 115, 91, 41. IR (KBr): 3305,2975, 2875, 1605, 1510, 1225, 1058 cm^{-1}. Anal. calcd for $C_{18}H_{19}NO_2$ (281.35): C, 76.84; H, 6.81; N, 4.98. Found: C, 76.86; H, 6.83; N, 4.99.

4-(4-Fluorophenyl)-2,3,3a,4,5,9b-hexahydro furo[3,2-c]quinoline. White solid, mp 173–1758C; 1H NMR (CDCl3): d 1.50 (m, 1H), 2.10–2.15 (m, 1H), 2.60–2.80 (m, 1H), 3.65–3.80 (m, 3H), 4.64 (d, J¼2.5 Hz, 1H), 5.20 (d, J¼8.0 Hz, 1H), 6.50 (d, J¼8.0 Hz, 1H), 6.78 (t, J¼8.0 Hz, 1H), 7.05 (m, 3H), 7.30 (m, 1H), 7.40 (m,2H). EIMS: m/z: 269Mþ, 240, 224, 198, 174, 130, 117, 77, 39. IR (KBr): 3315, 2976, 2880, 1606, 1508, 1223, 1155, 1059 cm^{-1}. Anal. calcd for $C_{17}H_{16}FNO$ (269.31): C, 75.82; H, 5.99; F, 7.05; N, 5.20. Found: C, 75.85; H, 6.00; F, 7.07; N, 5.22.

4-(4-Chlorophenyl)-8-methyl-2,3,3a,4,5,9bhexahydrofuro[3,2-c]quinoline. White solid, mp 148– 1498C; 1H NMR (CDCl3): d 1.50 (m, 1H), 2.20 (m, 1H), 2.35 (s, 3H), 2.64 (m, 1H), 3.60 (brs, NH, 1H), 3.72 (m, 1H), 3.80 (m, 1H), 4.60 (d, J¼2.1 Hz, 1H), 5.20 (d, J¼8.0 Hz,

1H), 6.50 (d, J¼8.0 Hz, 1H), 6.85 (dd, J¼8.0, 2.1 Hz, 1H), 7.10 (d, J¼2.1 Hz, 1H), 7.35 (d, J¼8.0 Hz, 2H), 7.40 (d, J¼8.0 Hz, 2H). EIMS: m/z: 299 Mþ, 254, 188, 160, 144,

115, 77. IR (KBr): 3345, 2991, 2878, 1610, 1493 cm^{-1}.

5-Phenyl-3,4,4a,5,6,10b-hexahydro-2Hpyrano[3,2-c]quinoline.

White solid, mp 129–1308C (lit,5b mp

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128.8–1318C); 1H NMR (CDCl3): d 1.25 (m, 1H), 1.50–1.70 (m, 3H), 2.15–2.20 (m, 1H), 3.40 (dt, 1H, J¼11.3, 2.4 Hz), 3.55 (dd, 1H, J¼11.3, 2.4 Hz), 3.80 (brs, 1H, NH), 4.70 (d, J¼2.7 Hz, 1H), 5.30 (d, J¼5.6 Hz, 1H), 6.55 (d, J¼8.0 Hz, 1H), 6.78 (t, J¼8.0 Hz, 1H), 7.05 (t, J¼7.8 Hz, 1H), 7.25–7.45 (m, 6H); 13C NMR (CDCl3) d: 18.2, 25.7, 39.0, 59.3, 60.7, 72.8, 114.4, 118.0, 120.4, 126.9, 127.5, 127.7, 128.0, 128.4, 141.2, 145.2. EIMS: m/z: 265 Mþ, 234, 220, 194, 129, 117, 91, 77. IR (KBr): nmax: 3340, 2970, 2850, 1610, 1490, 1090 cm^{-1}. Anal. calcd for $C_{18}H_{19}NO$ (265.35): C, 81.48; H, 7.22; N, 5.28. Found: C, 81.50; H, 7.24; N, 5.30. 4.1.9

5-(4-Fluorophenyl)-3,4,4a,5,6,10b-hexahydro- 2H-pyrano[3,2-c]quinoline.

White solid, mp 174– 1758C; 1H NMR (CDCl3): d 1.30 (m, 1H), 1.45–1.60 (m, 3H), 2.12 (m, 1H), 3.40 (dt, J¼11.5, 2.5 Hz, 1H), 3.56 (dd, J¼11.5, 2.5 Hz, 1H), 3.75 (brs, 1H, NH), 4.65 (d, J¼2.7 Hz, 1H), 5.28 (d, J¼5.7 Hz, 1H), 6.52 (d, J¼8.0 Hz, 1H), 6.75 (dd, J¼8.0, 2.5 Hz, 1H), 7.05 (m, 3H), 7.40 (m, 3H). EIMS: m/z: 283 Mþ, 239, 225, 198, 150, 148, 91. IR (KBr): nmax:

3325, 2945, 2860, 1608, 1490, 1252, 1081 cm^{-1}. Anal. calcd for $C_{18}H_{18}FNO$ (283.34): C, 76.30; H, 6.40; F, 6.71; N, 4.94. Found: C, 76.32; H, 6.44; F, 6.72; N, 4.95. 4.1.11.

7-Methyl-5-phenyl-3,4,4a,5,6,10b-hexahydro- 2H-pyrano[3,2-c]quinoline.

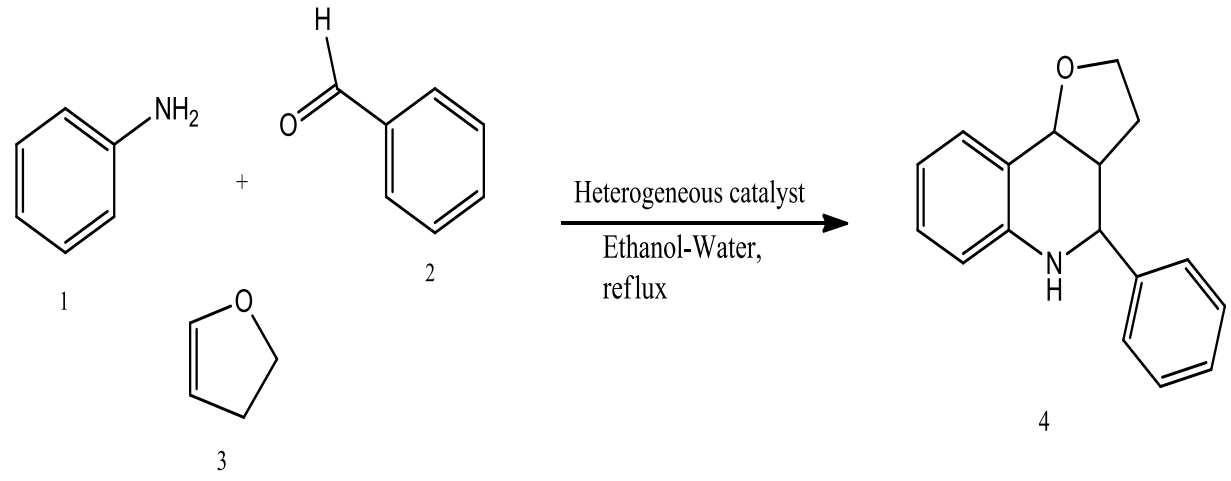
White solid, mp 142–1438C (lit,5b mp 143–1448C); 1H NMR (CDCl3): d 1.25 (m, 1H), 1.35 1.50 (m, 4H), 2.10 (s, 3H), 3.34 (dt, 1H, J¼11.3, 2.4 Hz), 3.50 (dd, 1H, J¼11.3, 2.4 Hz), 3.55 (brs, 1H, NH), 4.62 (d, J¼2.5 Hz, 1H), 5.30 (d, J¼5.2 Hz, 1H), 6.70 (t, J¼7.8 Hz, 1H), 6.90 (dd, J¼7.8, 0.7 Hz, 1H), 7.20–7.40 (m, 6H). 13C NMR (CDCl3) d: 17.4, 18.0, 25.3, 38.6, 59.3, 60.6 73.4, 117.8, 119.0, 121.6, 125.3, 126.9, 127.5, 128.9, 129.2, 141.0, 143.5. EIMS: m/z: 279 Mþ, 260, 220, 184, 155, 144, 104, 91, 65. IR (KBr): 3345, 2970, 2845, 1610, 1509, 1030 cm^{-1}. Anal. calcd for $C_{19}H_{21}NO$ (279.38): C, 81.68; H, 7.58; N, 5.01. Found: C, 81.70; H, 7.61; N, 5.02.

3. Result and Discussion

In the present work, we reported highly efficient synthesis of pyranoquinoline from substituted aniline, benzaldehyde, and 2,3dihydrofuran or by using heterogeneous catalyst $FeCl_3$ in ethanol-water as green solvent at reflux temperature.

In order to optimization of catalyst, we also tried different catalyst, out of them $FeCl_3$ is found to be better catalyst for synthesis of 4. The reaction is also carried out at solvent free condition but yield was low and requires more reaction time.

Scheme 1:



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In addition we studied, effect of different solvent on synthesis of **4** by using optimized percentage weight of catalyst, the result was summarized in table **1**. Initially, synthesis of pyranoquinoline is carried out in toluene as solvent by using 10 wt% $FeCl_3$ catalyst at room temperature results into 40% conversion with 24% yield. The reaction in methanol and acetonitrile are efficient for conversion but poor yield as 40, 60% (Entry 2,3).Tetrahydrofuran and 1,4-dioxane were found to be inferior solvents in which reaction slows down even after prolonged reaction time. However in Ethanol-Water by using same catalyst gives efficient conversion with high yield at reflux temperature (Entry 7). Experimental results indicates solvent enhances catalytic activity, thus the given protocol for synthesis of pyranoquinoline in green solvent is environmentally benign.

Table-1 Effect of different solvent on synthesis of pyranoquinoline using $FeCl_3$catalyst

Sr. No.	Solvent	$FeCl_3$	Time(min)	Conversion(%)	Yield(%)
1	Toulene	10 Wt %	120	40	24
2	Methanol	10 Wt %	120	60	40
3	Acetonitrile	10 Wt %	120	85	60
4	THF	10 Wt %	120	55	38
5	1,4-dioxane	10 Wt %	120	48	30
6	Ethanol	10 Wt %	120	100	70
7	Ethanol-Water	10 Wt %	120	100	85

Scheme: 2

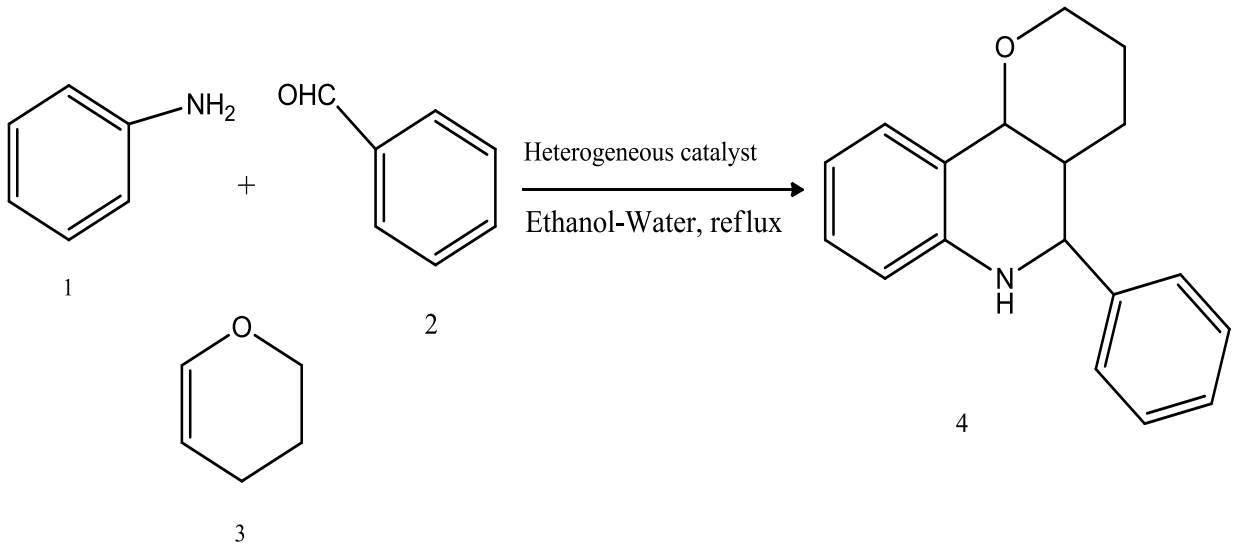

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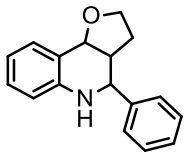
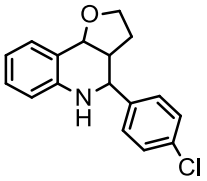
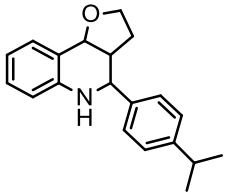
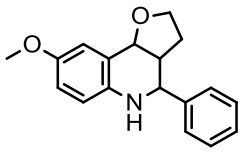
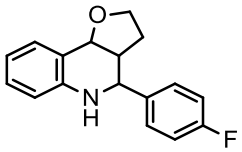
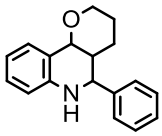
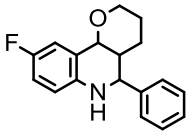
Table-2 : Synthesis of Furano, Pyranoquinoline by using ferric chloride in green solvent at reflux temperature.

Sr.No.	Reactant	Time	Product	Yield
1	Aniline, Benzaldehyde and 2,3-dihydrofuran	120		85
2	Aniline,4-chlorobenzaldehyde and 2,3-dihydrofuran	125		82
3	Aniline,4-isopropylbenzaldehyde and 2,3-dihydrofuran	129		85
4	p-Methoxyaniline, Benzaldehyde and 2,3-dihydrofuran	140		75
5	Aniline, Benzaldehyde and 2,3-dihydrofuran	140		78
6	Aniline, Benzaldehyde and 2,3-dihydropyran	120		82
7	p-Fluroaniline, Benzaldehyde and 2,3-dihydrofuran	130		79

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