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An efficient and green protocol for synthesis of 3,3'-arylmethylene-bis(4-hydroxyquinolin-2(1H)-ones) using potassium phthalimide as reusable catalyst

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- ✓ Aromatic aldehyde

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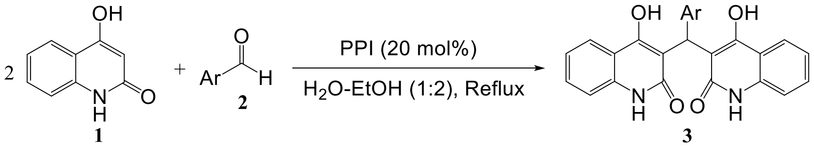
Abstract

A simple, efficient and eco-friendly procedure has been developed using potassium phthalimide as catalyst for the synthesis of 3,3'-arylmethylene-bis(4-hydroxyquinolin-2(1H)-ones) in aqueous ethanol. The present methodology offers several advantages such as operational simplicity, use of potassium phthalimide as a green, non-toxic, inexpensive and reusable catalyst, high yields and environmentally benign reaction conditions.

1. Introduction

Quinoline derivatives have shown good antiasthmatic,[1] antibacterial,[2] and anti-inflammatory [3] activities. Synthesis of bis(4-hydroxyquinolin-2(1H)-ones)derivatives has been reported by condensation of aryl aldehyde and 4-hydroxyquinolin-2-one in ethyl alcohol catalyzed by KF/Al_2O_3 [4] and in ethylene alcohol under microwave irradiation [5]. KF/Al_2O_3 gave good results but lack of recyclability and its corrosive nature limits its application[4]. Microwave irradiation promoted reaction does not need catalyst[5]. However, use of special apparatus hinders its industrial applications. Hence, the development of facile and environment friendly methods is still required for green and sustainable chemistry.

Potassium phthalimide (PPI) has been utilized as a green and commercially organocatalyst in the synthesis of Biginelli-type compounds [6], dihydropyrano[3,2-c]chromenes [7], 4H-chromens and 4H-pyrans [8], 2-amino-4H-benzo[h]chromene and 3-amino-1H-benzo[f]chromene derivatives [9]. Ethanol-water is considered to be relatively eco-friendly solvent [10-13]. In this paper, we report a simple, efficient and eco-friendly method for synthesis of bis(4-hydroxyquinolin-2(1H)-ones)derivatives using different aromatic aldehydes and 4-hydroxyquinolin-2(1H)-one in the presence of potassium phthalimide under reflux in aqueous ethanol (Scheme 1). Separation of the product and recycling of the catalyst were easily achieved six times without significant loss of activity.



Scheme 1 Synthesis of 3,3'-arylmethylene-bis(4-hydroxyquinolin-2(1H)-ones) catalyzed by potassium phthalimide

2. Materials and methods

2.1. General Methods

Melting points were measured on a digital melting point apparatus and were uncorrected. Fourier-transform infrared spectra were obtained on a Nexus 470 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Bruker Avance III 400 with tetramethylsilane as internal standard. All chemicals used were commercial products.

2.2. General experimental procedure

A mixture of 4-hydroxyquinolin-2(1H)-one (4 mmol), aldehyde (2 mmol) and potassium phthalimide (0.4 mmol) in water-ethanol (V:V=1:2, 10 mL) was stirred at reflux temperature. After completion of the reaction confirmed by thin layer chromatography, the reaction mixture was cooled to room temperature. The precipitated solid was filtered, washed with water-ethanol (V:V=1:2) and crystallized from dimethylformamide-water(V:V=6:1) to afford the products. Products obtained are all known compounds and were identified by comparing of their physical and spectra data with the reported ones.

2.3. Spectral data of products

3,3'-(2,4-Dichlorophenyl)methylene-bis(4-hydroxyquinolin-2(1H)-ones) (3a)

IR (KBr) ν: 3077, 1643, 1596, 1549, 1454, 1476, 1411, 1331, 1255, 1164, 1114, 886, 767 cm^{-1}.^{1}H NMR (DMSO-d_6) δ: 6.48 (s, 1H, CH), 7.33 (d, J=8.0 Hz, 1H, Ar-H), 7.41 (d, J=8.0 Hz, 1H, Ar-H), 7.44-7.49 (m, 2H, Ar-H), 7.51-7.58 (m, 3H, Ar-H), 7.65 (d, J=7.6 Hz, 2H,Ar-H), 7.82 (d, J=8.0 Hz, 2H,Ar-H), 12.24(s, 2H, 2NH), 12.74(s, 1H, OH), 13.11(s, 1H, OH).

3,3'-(3-Nitrophenyl)methylene-bis(4-hydroxyquinolin-2(1H)-ones) (3b)

IR (KBr) ν: 3059, 1639, 1597, 1529, 1465, 1378, 1335, 1259, 1094,809, 798 cm^{-1}.^{1}H NMR (DMSO-d_6)δ: 6.35(s, 1H, CH), 7.35-7.38 (m, 2H, Ar-H), 7.49 (d, J＝8.0 Hz, 2H, Ar-H), 7.58-7.69 (m, 4H, Ar-H), 7.92 (s, 1H, ArH), 8.04 (d, J＝7.6 Hz, 2H, Ar-H), 8.15 (d, J＝7.6 Hz, 1H, Ar-H), 12.35 (s, 2H, 2NH), 12.97 (s, 2H, 2OH).

3,3'-(4-Chlorophenyl)methylene-bis(4-hydroxyquinolin-2(1H)-ones) (3c)

IR (KBr) ν: 3073, 1645, 1611, 1493, 1392, 1326, 1211, 1148, 1092, 898, 836, 771 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 6.21(s, 1H, CH), 7.17 (d, J＝8.4 Hz, 2H, Ar-H), 7.33-7.36 (m, 4H, Ar-H), 7.49 (d, J＝8.4 Hz, Ar-H, 2H), 7.64-7.67 (m, 2H, Ar-H), 7.99 (s, 2H, Ar-H), 12.27 (s, 2H, 2NH), 12.74 (s,1H, OH), 13.15 (s, 1H, OH).

3,3'-(2-Chlorophenyl)methylene-bis(4-hydroxyquinolin-2(1H)-ones) (3d)

IR (KBr) ν: 3079, 1641, 1594, 1505, 1406, 1338, 1276, 1158, 1277, 1046, 846, 759 cm^{-1}.^{1}H NMR (DMSO-d_6) δ: 6.41(s, 1H, CH), 7.32-7.47 (m, 8H, Ar-H), 7.61 (d, J＝7.6 Hz, 2H, Ar-H), 7.98 (d, J＝8.0 Hz, 2H, Ar-H), 12.17 (s, 2H, 2NH), 12.78 (s, 1H, OH), 13.09 (s,1H, OH), 13.18 (s, 1H, OH).

3,3'-(4-Bromophenyl)methylene-bis(4-hydroxyquinolin-2(1H)-ones) (3e)

IR (KBr) ν: 3078, 1641, 1589, 1473, 1405, 1328, 1269, 1157, 1276, 1037, 846, 749 cm^{-1}.^{1}H NMR (DMSO-d_6) δ: 6.17 (s, 1H, CH), 7.09 (d, J＝8.0 Hz, 2H, Ar-H), 7.35 (d, J＝8.0 Hz, 2H, Ar-H), 7.39-7.48 (m, 4H, Ar-H), 7.65 (d, J＝7.6 Hz, 2H, Ar-H), 7.99 (d, J＝8.0 Hz, 2H, Ar-H), 12.29 (s, 2H, 2NH), 12.78 (s, 1H, OH), 13.16 (s, 1H, OH).

3,3'-(4-Fluorophenyl)methylene-bis(4-hydroxyquinolin-2(1H)-ones)(3f)

IR (KBr) ν: 3078, 1649, 1606, 1508, 1396, 1327, 1228, 1157, 1276, 1033, 854, 758 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 6.19 (s, 1H, CH), 7.07-7.17 (m, 4H, Ar-H), 7.35 (d, J＝8.0 Hz, 2H, Ar-H), 7.35-7.48 (m, 2H, Ar-H), 7.61 (d, J＝7.6 Hz, 2H, Ar-H), 7.98 (d, J＝8.0 Hz, 2H, Ar-H), 12.27 (s, 2H, 2NH), 12.78 (s, 1H, OH), 13.06 (s, 1H, OH).

3,3'-(4-Methoxyphenyl)methylene-bis(4-hydroxyquinolin-2(1H)-ones)(3g)

IR (KBr) ν: 3075, 1653, 1612, 1519, 1485, 1418, 1345, 1225, 1191, 1135, 1049, 876, 775 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 3.75(s, 3H, CH_3O), 6.16 (s, 1H, CH), 6.86 (d, J＝8.4 Hz, 2H, Ar-H), 7.05 (d, J＝8.4 Hz, 2H, Ar-H), 7.32-7.35 (m, 2H,Ar-H), 7.47 (d, J＝8.0 Hz, 2H, Ar-H), 7.62-7.66 (m, 2H, Ar-H), 7.99 (s, 2H, Ar-H), 12.25 (s, 2H, 2NH), 12.71 (s, 1H, OH), 13.17 (s, 1H, OH).

3,3'-(4-Dimethylaminophenyl)methylene-bis(4-hydroxyquinolin-2(1H)-ones) (3h)

IR (KBr) ν: 3072, 1653, 1611, 1527, 1485, 1341, 1330, 1293, 1226,1157, 1125, 973, 865, 774cm^{-1}.^{1}H NMR (DMSO-d_6) δ: 2.87(s, 6H, 2CH_3), 6.13 (s, 1H, CH), 6.67 (d, J＝8.8 Hz, 2H, Ar-H), 6.95 (d, J＝8.8 Hz, 2H, Ar-H), 7.31-7.35 (m, 2H, Ar-H), 7.47 (d, J＝8.0 Hz, 2H, Ar-H), 7.61-7.65 (m, 2H, Ar-H), 7.97 (s, 2H, Ar-H), 12.15 (s, 1H, NH), 12.26 (s, 1H,NH), 12.68 (s, 1H, OH), 13.17 (s, 1H, OH).

3. Results and discussion

To optimize the reaction conditions, the reaction of 2,4-dichlorobenzaldehyde and 4-hydroxyquinolin-2(1H)-one was used as a model reaction. The reaction was examined in various solvents using 10 mol% potassium phthalimide as catalyst. The best results were obtained when H_2O-EtOH (1:2) was used as a solvent at reflux (Table 1, entry 8). In order to determine the optimal amount of potassium phthalimide, model reaction was carried out at reflux in H_2O-EtOH (V:V=1:2). The optimal amount of potassium phthalimide was 20 mol % (based on 2,4-dichlorobenzaldehyde). Extra amounts of the catalyst did not improve the yields. The product was not obtained even after reflux for 6 h in the absence of the catalyst (Table 1, entry 3) indicating that the catalyst is necessary for the reaction.

Table 1: Optimization of reaction conditions [a]

Entry	Solvent	potassiumphthalimide (mol%)	Time (min)	Yield[b] (%)
1	H_2O	10	300	-
2	EtOH	10	300	78
3	H_2O-EtOH (1:1)	-	360	-
4	H_2O-EtOH (1:1)	10	300	88
5	H_2O-EtOH (1:1)	15	150	89
6	H_2O-EtOH (1:1)	20	90	88
7	H_2O-EtOH (1:1)	30	90	88
8	H_2O-EtOH (1:2)	10	150	88
9	H_2O-EtOH (1:3)	10	180	88
10	H_2O-EtOH (2:1)	10	760	87
11	H_2O-EtOH (1:2)	15	90	86
12	H_2O-EtOH (1:2)	20	75	88
13	H_2O-EtOH (1:2)	30	75	86

[a] Reaction conditions: 4-hydroxyquinolin-2(1H)-one (4 mmol), 2,4-dichlorobenzaldehyde (2 mmol), solvent (10 mL).
[b] Isolated yields.

To explore the generality and scope of the catalyst, we extended our study using potassium phthalimide (20 mol %) in H_2O-EtOH (V:V=1:2) with different aromatic aldehydes to prepare a series of 3,3'-arylmethylene-bis(4-hydroxyquinolin-2(1H)-ones) derivatives (Table 2). Various aromatic aldehydes containing electron-withdrawing substituents, electron-donating substituents were utilized successfully in the reaction, and gave the corresponding products in high yields.

Table 2: Potassium phthalimide catalyzed synthesis of 3,3'-arylmethylene-bis(4-hydroxyquinolin-2(1H)-ones)[a]

Product	Ar	Time (min)	Yield [b] (%)	Mp (°C)
3a	2,4-$Cl_2C_6H_3$	75	88	>300 (lit [4-5]> 300)
3b	3-$NO_2C_6H_4$	120	86	>300 (lit [4-5]> 300)
3c	4-ClC_6H_4	20	85	>300 (lit [4-5]> 300)
3d	2-ClC_6H_4	120	89	>300 (lit [4-5]> 300)
3e	4-BrC_6H_4	25	86	>300 (lit [4-5]> 300)
3f	4-FC_6H_4	15	79	>300 (lit [4-5]> 300)
3g	4-$CH_3OC_6H_4$	20	76	>300 (lit [4-5]> 300)
3h	4-$N(CH_3)_2C_6H_4$	20	69	>300 (lit [4-5]> 300)

[a] Reaction conditions: 4-hydroxyquinolin-2(1H)-one (4 mmol), aldehyde (2 mmol), potassium phthalimide (20 mol %), H_2O-EtOH (V:V=1:2, 10 mL), reflux.
[b] Isolated yields.

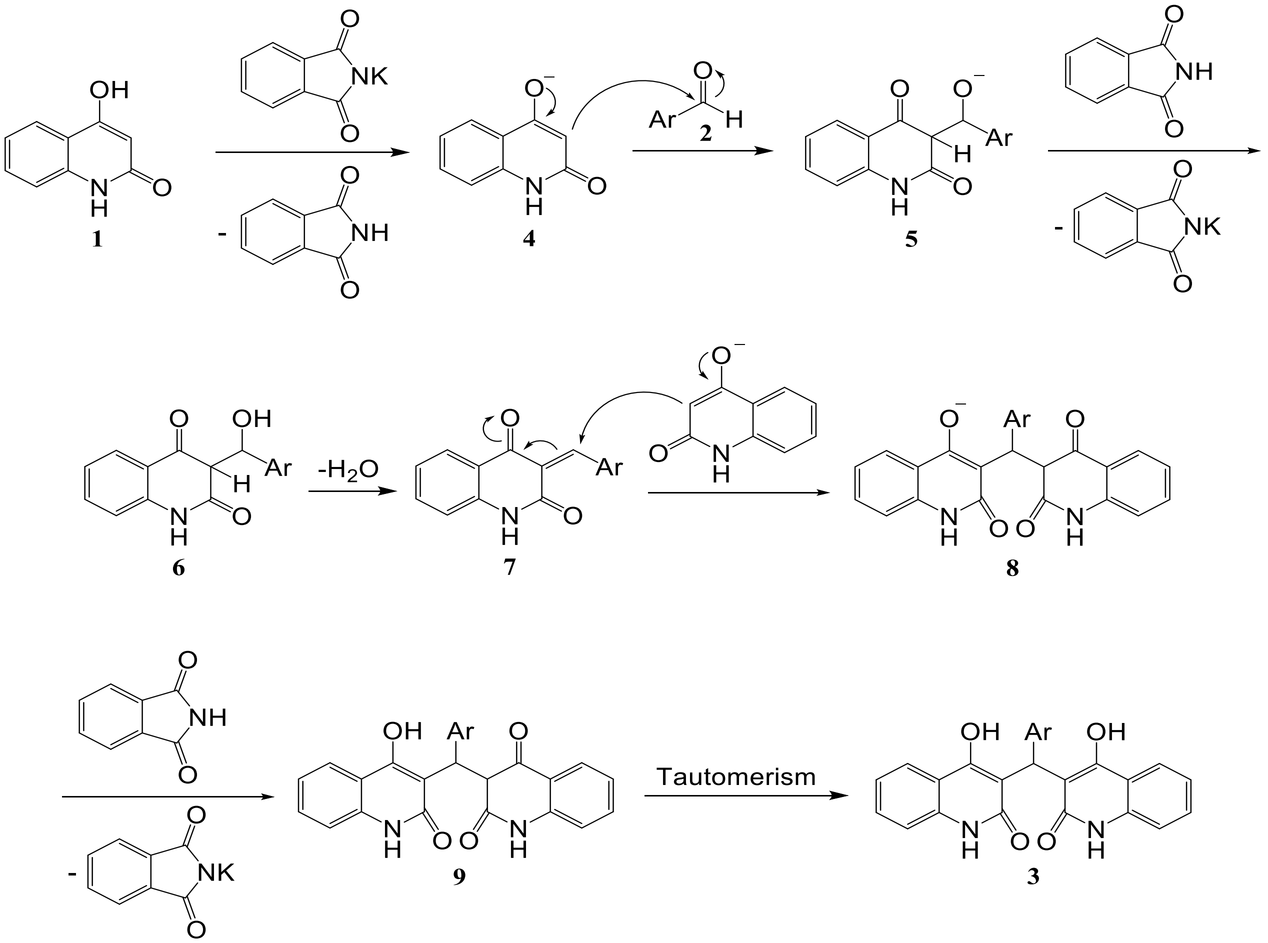
The reusability of the catalyst was tested upon the reaction of 4-hydroxyquinolin-2(1H)-one (4 mmol) and 4-chlorobenzaldehyde (2 mmol). After completion of the reaction confirmed by thin layer chromatography, the reaction mixture was cooled to room temperature and filtered to separate the products from the catalyst. The filtrate containing of potassium phthalimide was reused directly in the next run without any treatment. As can be seen from Table 3, the catalyst aqueous-ethanol solutions could be reused at least six times without significant loss of activity.

Table 3: Reusability of catalyst

Run	Time (min)	Yield[b] (%)
1	20	85
2	20	86
3	20	85
4	20	83
5	20	82
6	35	81
7	50	80

[a] Reaction conditions: 4-hydroxyquinolin-2(1H)-one (4 mmol), 4-chlorobenzaldehyde (2 mmol), potassium phthalimide (20 mol %), H_2O-EtOH (V:V=1:2, 10 mL), reflux.

[b] Isolated yields.



Scheme 2 Plausible mechanism for the synthesis of 3,3'-arylmethylene-bis(4-hydroxyquinolin-2(1H)-ones) catalyzed by potassium phthalimide

A plausible mechanism for the synthesis of 3,3'-arylmethylene-bis(4-hydroxyquinolin-2(1H)-ones) in the presence of potassium phthalimide is exhibited in Scheme 2. The transformation involves a Knoevenagel condensation of 4-hydroxyquinolin-2(1H)-one with the aldehyde followed by a Michael addition with another molecule of 4-hydroxyquinolin-2(1H)-one.

Conclusion

In conclusion, we have reported a simple, efficient and green protocol for the synthesis of 3,3'-arylmethylene-bis(4-hydroxyquinolin-2(1H)-ones) in aqueous ethanol. The method offers several advantages such as operational simplicity, use of potassium phthalimide as a green, non-toxic, inexpensive and reusable catalyst, high yields and environmentally benign reaction conditions.

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