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ARTICLE TYPE

Rhodium-Catalyzed Synthesis of Quinolines and Imines under Mild Condition

Dilip Kumar T. Yadav and Bhalchandra M. Bhanage*

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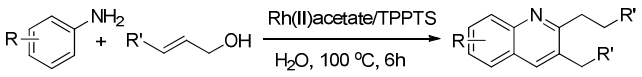
An environmentally benign protocol for the synthesis of quinolines in aqueous medium by using Rh(II)acetate/TPPTS recyclable catalytic system has been developed. The anilines were reacted smoothly with allyl alcohols furnishing the corresponding quinolines in moderate to good yields. This catalytic system was recycled up to five runs without much loss in its catalytic activity. Furthermore, imines were also synthesized from benzylamines in moderate to good yields.

Introduction

Quinolines are important class of compounds which display attractive applications in pharmaceuticals, agrochemicals, fungicides, herbicides, complexing agents and dyes.[1] Furthermore, substituted quinoline structural frameworks are often found in many biological active molecules and they exhibits antibacterial,[2] antimalarial,[3] antiinflammatory,[4] antiprotozoan,[5] antiasthmatic,[6] antituberculosis,[7] antihypertensive,[8] anticancer,[9] anti-HIV,[10] and antihelmintic activities.[11] Moreover, quinolines are also vital synthons for the synthesis of many important materials such as nano-meso structures and polymers which are investigated for applications in electronics, optoelectronics and nonlinear optics.[12] Hence, the development of simple and efficient protocol for the synthesis of quinolines has been the subject of continued interest from the several decades.

Traditionally, quinolines were synthesized by the Skraup reaction,[13] the Conrad-Limpach reaction,[14] the Pfitzinger reaction,[15] the Doebner-Von Miller reaction,[16] and the Friedlaender reaction.[17] However, these reactions suffer from one or more drawbacks such as use of environmentally unfriendly strong acids or bases, high temperatures, low yields and harsh reaction conditions. The other alternative methods for the synthesis of quinolines by transition metal-catalyzed process were also reported in the literature. Some research groups have reported the rhodium complex catalyzed reaction of aniline with aliphatic aldehyde,[18] aliphatic olefin,[19] styrene,[20] and the reaction of nitrobenzene with aliphatic alcohol[21] for the synthesis of quinolines. Subsequently, other transition metal precursors of Ru,[22] Pd,[23] Ni,[24] Co,[25] and Fe[26] were also developed for the quinolines synthesis. Despite the advances in methodology for the quinoline synthesis, most of the reported protocols have one or more shortcomings such as use of hazardous organic solvents, harsh reaction conditions, limited functional-group tolerance and the homogeneous non-recyclable catalytic system which has the problem of catalyst-product separation thereby limits the attractiveness of these transformations for their general applications. Thus, to develop an economical and sustainable methodology for the quinolines synthesis which should operate under environmentally favourable condition remains an active area of research.

Now a days, the use of water as a reaction media for organic reactions have been made attention, as water is an inexpensive, readily available, safe and non-toxic solvent which provides remarkable advantages over common organic solvents from environmental and economic points of view.[27] Hence, the progress towards the development of new water-soluble catalytic protocol for the quinoline synthesis which allows an easy separation of the catalyst from product, and recyclability of aqueous solution containing the catalyst by employing water as a reaction media could be the answer for the future of green chemistry. In continuation of our ongoing research on the development of a new facile protocol in water as a green reaction media.[28] Herein, we report a simple and efficient recyclable rhodium catalyzed protocol for quinolines synthesis in water using the triphenylphosphine trisulfonate sodium salt (TPPTS) (Scheme 1).



Scheme 1: Rh(II)acetate /TPPTS catalyzed synthesis of quinolines.

Results and discussion

Initially to optimize the reaction conditions aniline (**1a**) and allyl alcohol (**2a**) was chosen as a model substrate for the rhodium-catalyzed synthesis of quinoline derivative. A series of experiments were performed in order to study the effect of various reaction parameters such as catalyst screening, catalyst loading, time and temperature for the synthesis of quinolines (Table 1). Firstly, we have screened various rhodium precursors such as $RhCl_3$, $Rh(PPh_3)_3Cl$, Rh(COD)Cl and Rh(II)acetate for

*Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai-400019. India.
Tel.: +91-22-33612601; fax: +91-22-33611020;
E-mail: bm.bhanage@gmail.com, bm.bhanage@ictmumbai.edu.in

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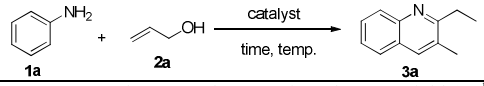
the synthesis of 2-ethyl-3-methylquinoline (**3a**) (Table 1, entries 1–4) and it was found that Rh(II)acetate furnished the best yield of the desired product **3a** and hence was used for further studies (Table 1, entry 4). However, other rhodium precursors like $RhCl_3$, $Rh(PPh_3)_3Cl$ and Rh(COD)Cl provided **3a** in moderate yields (Table 1, entries 1–3). However, the reaction of **1a** with **2a** did not give desired product **3a** in the absence of the catalyst which shows that catalyst is necessary for the progress of reaction (Table 1, entry 5). Furthermore, when the reaction was performed in the absence of TPPTS ligands, formation of **3a** was observed in low yield (Table 1, entry 6). Next, we have studied the effect of catalyst loading and it was observed that 0.03 mmol of Rh(II) acetate gave **3a** in good yield (Table 1, entry 7). Furthermore, we have also studied the effect of TPPTS loading and it was observed that 0.06 mmol of it gave **3a** in 82% yield (Table 1, entry 8). Subsequently, we have studied the effect of reaction time and it was found that 6 h was the optimum time required for completion of the reaction and further increase in time has found no effect on reaction outcome (Table 1, entry 9). Furthermore, we have also examined the temperature effect on the formation of **3a** and it was found that increase in temperature has no effect on reaction outcome whereas with decrease in reaction temperature from 100 °C to 90 °C decrease in yield of **3a** observed (Table 1, entries 10 and 11).

Table 1: Optimization of the reaction conditions[a]



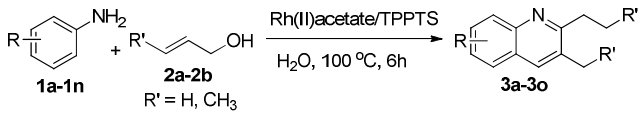
1a 2a 3a

Entry	Catalyst (mmol)	Time (h)	Yield (%)[b] **3a**
1	$RhCl_3$	4	64
2	$Rh(PPh_3)_3Cl$	4	63
3	Rh(COD)Cl	4	67
4	Rh(II)acetate	4	72
5	-	4	-
6[c]	Rh(II)acetate	4	57
7	Rh(II)acetate (0.03)	4	79
8[d]	Rh(II)acetate (0.03)	4	82
9[d]	Rh(II)acetate (0.03)	6	88
10[d,e]	Rh(II)acetate (0.03)	6	88
11[d,f]	Rh(II)acetate (0.03)	6	78

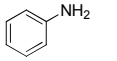
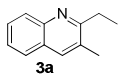
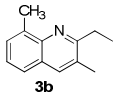
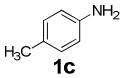
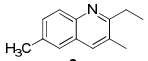
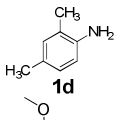
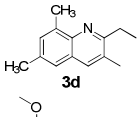
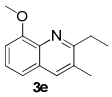
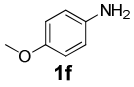
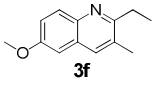
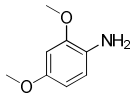
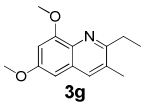
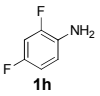
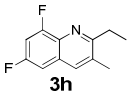
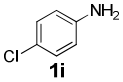
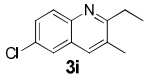
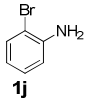
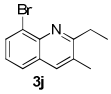
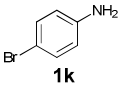
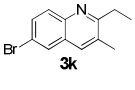
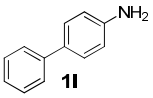
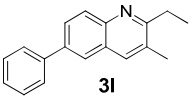
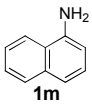
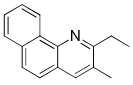
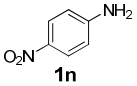
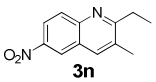
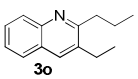
[a] Reaction conditions: **1a** (1.0 mmol), **2a** (2.5 mmol), Catalyst (0.02 mmol), TPPTS (0.04 mmol), water (4 mL), 100 °C. [b] GC yield. [c] No TPPTS. [d] TPPTS (0.06 mmol). [e] 110 °C. [f] 90 °C.

With these optimized reaction conditions, we have studied the scope and limitations of present methodology for the preparation of different kinds of structurally diverse quinolines. Firstly, the reaction of **1a** with **2a** provided corresponding product **3a** in 86% isolated yield (Table 2, entry 1). Next, it was found that *ortho*-substituted electron donating aniline derivative (**1b** and **1e**) shows the steric effect and furnished the corresponding product **3b** and **3e** in moderate yields (Table 2, entries 2 and 5). The reaction of *p*-substituted and disubstituted electron donating anilines (–CH_3, –OMe) with **2a** provided the respective products **3c-3g** in good yields (Table 2, entries 3–4 and 6–7). Subsequently, aniline derivatives bearing halo-substituents (–F, –Cl, –Br) were also well tolerated under the present reaction conditions and afforded

Table 2: Substrate study for the synthesis of quinolines[a]



1a-1n 2a-2b R' = H, CH_3 3a-3o

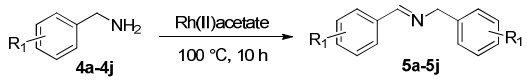
Entry	Aniline	Product	Yield (%)[b] 3
1	 1a	 3a	86
2	 1b	 3b	62
3	 1c	 3c	88
4	 1d	 3d	77
5	 1e	 3e	64
6	 1f	 3f	89
7	 1g	 3g	79
8	 1h	 3h	68
9	 1i	 3i	69
10	 1j	 3j	62
11	 1k	 3k	72
12	 1l	 3l	81
13	 1m	 3m	87
14	 1n	 3n	-
15	1a	 3o	74

[a] Reaction conditions: **1** (1 mmol), **2** (2.5 mmol), Rh(II)acetate (0.03 mmol), TPPTS (0.06 mmol), water (4 mL), 100 °C, 6 h, N_2 atmosphere. [b] isolated yield.

the corresponding products **3h–3k** in moderate yields (Table 2, entries 8–11). Furthermore, it was observed that when the simple aromatic ring of aniline was replaced by more hindered biphenyl and naphthyl groups, the respective quinolines were also obtained in good yields (Table 2, entries 12 and 13). However, the aniline bearing electron withdrawing group (-NO_2) did not furnished the corresponding product **3n** under the present reaction condition might be due to low nucleophilicity of such aniline (Table 2, entry 14). Furthermore, the reaction of **1a** with crotyl alcohol (**2b**) afforded respective product **3o** in 74% yield (Table 2, entry 15).

Imines have been used as valuable synthons for many advantageous chemicals such as nitrogen heterocycles, pharmaceuticals, fine chemicals, agricultural chemicals and in natural product synthetic applications.[29] In addition, imines also shows anti-bacterial anti-viral, anti-inflammatory and anti-fungal activities.[29e] Furthermore, imines also serve as a electrophiles in different type of reactions such as condensations, addition, cyclization, reductions and multi-component reactions.[30] Hence, developing newer methods for the synthesis of imines is an main task for the organic synthetic community. Consequently, much progress has been made for the imines synthesis such as self-condensation of primary amines with oxidants,[31] oxidation of secondary amines[32] and condensation of amines with alcohols.[33]

Table 3: Substrate study for the synthesis of imines[a]

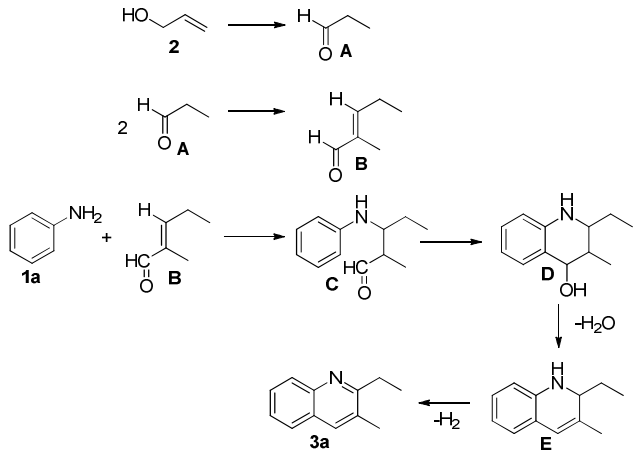


Entry	Benzylamine	Product	Yield (%)[b]
1	4a	5a	84
2	4b	5b	77
3	4c	5c	72
4	4d	5d	74
5	4e	5e	62
6	4f	5f	75
7	4g	5g	79
8	4h	5h	76
9	4i	5i	43
10	4j	5j	-

[a] Reaction conditions: **4** (2 mmol), Rh(II)acetate (0.03 mmol), 100 °C, 10 h. [b] isolated yield.

It was found that when benzyl amine (**4a**) was heated with Rh(II)acetate at 100 °C for 10 h under neat condition, it undergoes self condensation providing corresponding imine **5a** in good yield (Table 3, entry 1). Subsequently, the scope of imines synthesis was advance towards other benzyl amine derivatives (Table 3). It was observed that electron-rich benzylamine derivatives were well tolerated and affording respective products in good yields (Table 3, entries 2–5). Next, it is noteworthy that benzylamine bearing halo-substituents also performed well by providing corresponding imines in good yields (Table 3, entries 6–8), which could be used for further transformations along with the imine functionality. Subsequently, the heterocyclic benzyl amine gave respective imine **5i** in low yield (Table 3, entry 9). However, 1-phenylethanamine (**4j**) did not provide corresponding imine under the present reaction condition (Table 3, entry 10).

Based on our experimental observation and literature report,[18,34,35] we propose a plausible reaction mechanism for the synthesis of quinoline (Scheme 2). Initially, allyl alcohol (**2**) isomerized to corresponding propanal (**A**) in the presence of rhodium catalyst[34] which undergoes self aldol condensation to form corresponding unsaturated aldehyde (**B**).[35] The formation of unsaturated aldehyde (**B**) was confirmed by GC-MS. In the next step, aniline (**1a**) adds to compound **B** giving intermediate **C** which undergoes ring closure with elimination of water molecule forming intermediate **E** and in the last step dehydrogenation of intermediate **E** provides corresponding quinoline derivative (Scheme 2).



Scheme 2: Plausible mechanism for the synthesis of quinoline.

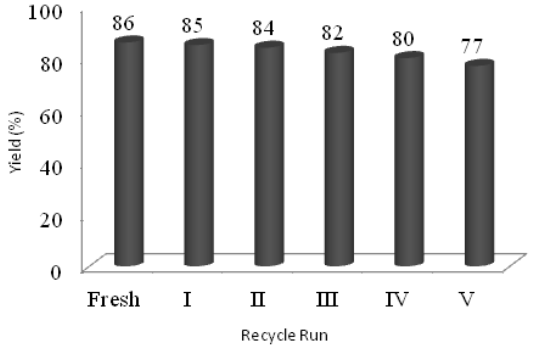


Fig. 1 Catalyst recyclability study. Reaction conditions: **1a** (1 mmol), **2a** (2.5 mmol), Rh(II)acetate (0.03 mmol), TPPTS (0.06

mmol), water (4 mL), 100 °C, 6 h, N_2 atmosphere. GC yield.

It is important to reveal that, catalyst separation and recyclability with homogeneous reactions have serious concern in industrial applications. So, in order to make present protocol more economical, here we have studied the reusability of developed catalytic system for a model reaction of **1a** with **2a** (Fig. 1). Here, we have extracted the product in organic phase from the catalyst containing aqueous phase and the catalyst containing aqueous phase was recycled for five times without much loss in its activity and the decrease in yield is might be due to handling loss during work up of the reaction.

Conclusion

In conclusion, we have developed a simple, highly efficient rhodium catalyzed aqueous phase recyclable methodology for the synthesis of quinolines from easily available amines and allyl alcohols. The various quinolines were efficiently synthesized by present method in moderate to good yields. The homogeneous water soluble Rh(II)acetate/TPPTS catalytic system could be reused for five runs after simple extraction of the product with ethyl acetate. Imines were also synthesized in good yields by rhodium catalyzed self-condensation of primary benzyl amines under mild reaction conditions. Due to the simplicity of developed protocol, it will cover a wide application in industry as well as academics. Thus, the developed protocol sounds to be highly efficient for the synthesis of quinolines and imines.

Experimental Section

A typical experimental procedure for the synthesis of quinoline from aniline and allyl alcohol:

In oven-dried sealed tube equipped with magnetic stirring bar, 4 mL of deionised water was charged and dry nitrogen gas was purged for 1 h. Next, **1a** (1 mmol), **2a** (2.5 mmol), rhodium acetate dimer (0.03 mmol) and triphenylphosphine trisulfonate sodium salt (0.06 mmol) were charged to the above degassed deionised water and then refluxed for 6 h under nitrogen atmosphere. On completion of reaction, it was cooled to room temperature and extracted with ethyl acetate (3×5 mL). The combined ethyl acetate layers were dried over anhydrous Na_2SO_4 and solvent was evaporated under reduce pressure. The obtained crude product was directly purified by column chromatography (silica gel, 100-200 mesh, PE–EtOAc) to afford the pure product. The identity of product was confirmed by ^1H and ^{13}C NMR spectroscopic analysis.

Recyclability study:

The reaction was performed as stated above in a typical experimental procedure and after completion of reaction, the reaction mixture was extracted with ethyl acetate and the aqueous phase containing catalyst was subjected further for catalyst recyclability study.

A typical experimental procedure for the synthesis of imine from benzyl amine:

The benzyl amine (**4a**, 2 mmol) and rhodium acetate dimer (0.03 mmol) were mixed in an oven-dried sealed tube with a magnetic stirrer bar and the reaction mixture was heated at 100 °C for 10 h. After cooling the reaction mixture to room temperature, the crude product was purified by column chromatography (basic alumina saturated with Et_3N, 100-200 mesh, PE) to provide the desired pure product. The identity of product was confirmed by comparison with those of authentic compounds from literature.

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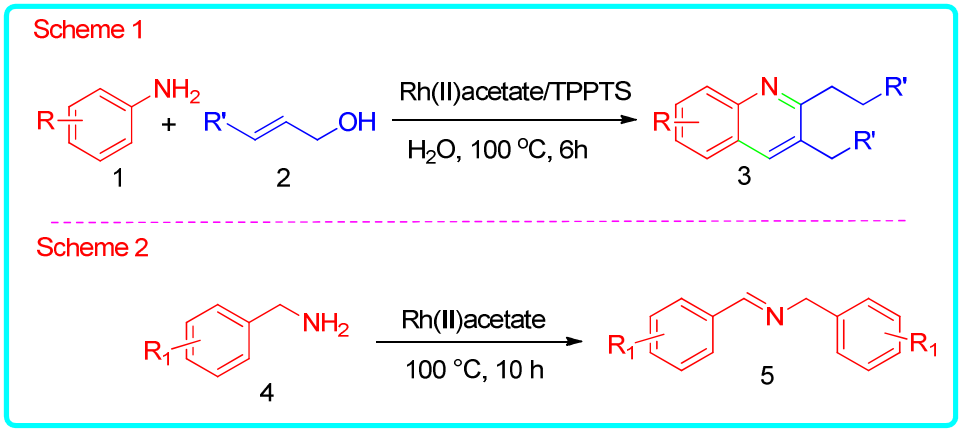
Rhodium-Catalyzed Synthesis of Quinolines and Imines under Mild Condition

Dilip Kumar T. Yadav and Bhalchandra M. Bhanage*

Department of Chemistry, Institute of Chemical Technology,
Matunga, Mumbai- 400019, India



A simple and efficient protocol for the synthesis of quinolines in aqueous medium by using Rh(II)acetate/TPPTS recyclable catalytic system has been developed. This catalytic system was recycled up to five runs without much loss in its catalytic activity. Furthermore, imines were also synthesized from benzylamines in moderate to good yields under solvent free condition.