Synthesis of Quinolines by Ruthenium-Catalyzed Heteroannulation of Anilines with 3-Amino-1-propanol

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Anilines react with 3-amino-1-propanol in dioxane in the presence of a catalytic amount of a ruthenium catalyst and tin(II) chloride dihydrate together with a hydrogen acceptor to afford the corresponding quinolines in moderate yields.

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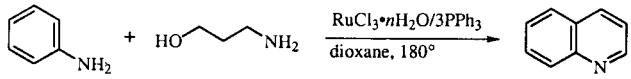
It is well-known that quinoline skeletons play an important role as an intermediate for the design of many antimalarial compounds. The Skraup and related quinoline syntheses are the most commonly used route for the construction of structural core of quinolines [1]. In contrast to the conventional synthesis, the formation of quinoline skeletons also has been attempted by a remarkable catalytic action of transition metal catalysts such as palladium [2-5], rhodium [6-11], ruthenium [12-17], and iron [18]. As part of our continuing studies on transition metal-catalyzed synthesis of *N*-heterocyclic compounds [19-21], we recently developed and reported a synthetic method for the formation of indoles [19b] and 2-ethyl-3-methylquinolines [22] from primary aromatic amines and tertiary amines under ruthenium-tin catalytic systems. It was suggested that both reactions proceed *via* amine exchange reactions between primary aromatic amines and tertiary amines. This finding prompted us to extend the similar ruthenium and tin-catalyzed heteroannulation of primary aromatic amines with another amines. We here report another ruthenium-catalyzed approach for the synthesis of 2,3,4-unsubstituted quinolines from primary aromatic amines and 3-amino-1-propanol.

The several results of the ruthenium-catalyzed heteroannulation between aniline (**1**) and 3-amino-1-propanol (**2**) under various conditions are listed in Table 1. We employed similar reaction systems such as the molar ratio of aniline (**1**) to 3-amino-1-propanol (**2**) and the amount of tin(II) chloride dihydrate as has been optimized in our recent ruthenium-catalyzed synthesis of indoles [19] and 2-ethyl-3-methylquinolines[22]. Treatment of aniline (1) with 3-amino-1-propanol (**2**) in dioxane under an argon atmosphere in the presence of a catalytic amount of ruthenium(III) chloride hydrate (4 mol% based on **2**) and triphenylphosphine (12 mol% based on **2**) together with tin(II) chloride dihydrate and acetone as a hydrogen acceptor at 180° for 20 hours afforded quinoline (**3**) in 47% yield (Scheme 1). These reactions condition was eventually shown to be the best for obtaining quinoline (**3**) (run 1). The yield of quinoline (**3**) was not improved by a longer reaction time (run 3). However, the reaction was accompanied by the formation of *N*-isopropylaniline (37% yield based on **2**) as a side product when acetone was used as a hydrogen acceptor. Because it is well-known that anilines react with aliphatic alcohols to give N-alkyiated anilines with a ruthenium catalyst [13, 23], this result indicates that acetone actually captures the hydrogen to form isopropyl alcohol under the catalytic reaction system.

Scheme 1



1 **2** **3**

On the other hand, the absence of either tin(II) chloride dihydrate or hydrogen acceptor stopped the reaction almost completely (runs 4-6). Thus, the coexistence of tin(II) chloride dihydrate and hydrogen acceptor was essential for the effective formation of quinolines. Various hydrogen acceptors such as nitrobenzene, acetophenone and cyclohexanone could be alternatively used, but the yield of quinoline (**3**) was lower than when acetone was used (runs 7-9). In addition, a variety of phosphorus chelating ligands such as bis-(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)-ethane and 1,3-bis(diphenylphosphino)propane combined with ruthenium(III) chloride dihydrate can also be used in place of triphenylphosphine, but the yield of quinoline (**3**) was generally lower than when triphenylphosphine was used (runs 10-12). Among catalysts examined, dichlorotris-(triphenylphosphine)ruthenium(II) exhibited nearly the same catalytic activity as $RuCl_3 \cdot nH_2O/PPh_3$ under the employed reaction conditions (run 13). However, other ruthenium catalyst precursors such as dihydridotetrakis-(triphenylphosphine)ruthenium(II) and dodecacarbonyl-triruthenium(0) were moderately effective for the formation of quinoline (**3**) (runs 14-15).

The present heteroannulation could also be applied to many primary aromatic amines under the above optimized conditions, several representative results being summarized in Table 2. All reactions were accompanied by the formation of the corresponding *N*-isopropylanilines as has been observed in the reaction of aniline with 3-amino-1-propanol (**2**). The quinoline yield was not decisively affected by the electronic nature and the position of the substituent on aniline. However, with chloroanilines having electron-withdrawing Cl substituent, the product yield was generally

Table 1

Ruthenium-Catalyzed Synthesis of Quinoline (3) under Various Conditions [a]

Run	Catalyst	Hydrogen acceptor	GLC yield [b]
1	$RuCl_3$•nH_2O/3PPh_3	acetone	47
2	$RuCl_3$•nH_2O/3PPh_3	acetone	21 [c]
3	$RuCl_3$•nH_2O/3PPh_3	acetone	48[d]
4	$RuCl_3$•nH_2O/3PPh_3	-	0 [e]
5	$RuCl_3$•nH_2O/3PPh_3	-	3
6	$RuCl_3$•nH_2O/3PPh_3	acetone	4 [e]
7	$RuCl_3$•nH_2O/3PPh_3	nitrobenzene	31
8	$RuCl_3$•nH_2O/3PPh_3	acetophenone	23
9	$RuCl_3$•nH_2O/3PPh_3	cyclohexanone	43
10	$RuCl_3$•nH_2O/1.5dppm	acetone	9
11	$RuCl_3$•nH_2O/1.5dppe	acetone	30
12	$RuCl_3$•nH_2O/1.5dppp	acetone	34
13	$RuCl_2(PPh_3)_3$	acetone	46
14	$Ru_3(CO)_{12}$	acetone	34
15	$RuH_2(PPh_3)_4$	acetone	32

[a] All reactions were carried out with aniline (1) (6 mmoles), 3-amino-1-propanol (2) (1 mmole), ruthenium catalyst (0.04 mmole), $SnCl_2$•$2H_2O$ and hydrogen acceptor (5 mmoles) in dioxane (10 ml) at 180° for 20 hours unless otherwise stated. [b] Based on 2. [c] For 5 hours. [d] For 40 hours. [e] In the absence of $SnCl_2$•$2H_2O$.

lower than that when anilines having electron-donating character were used. In contrast to our recent ruthenium-catalyzed synthesis of 2-ethyl-3-methylquinolines [22], in the case of *o*-toluidine the reaction also proceeded well toward 8-methylquinoline. In the case of *m*-toluidine, the product was obtained as a regioisomeric mixture, favoring the formation of 7-substituted isomer. Isomeric molar ratio between 5-methylquinoline and 7-methylquinoline was determined from the peak areas of the methyl protons in ^1H nmr spectrum. In the cases of two methyl substituted anilines such as 2,3-, 2,5- and 3,5-dimethylaniline, the reaction also proceeded irrespective of the position of methyl substituents and the corresponding quinolines were obtained in good yields.

Although the details of the present heteroannulation pathway are not yet clear, a possible pathway is shown in Scheme 2. The reaction seems to proceed via an initial formation of *N*-phenyl-3-amino-1-propanol (**4**) by amine exchange reaction [24] between aniline (**1**) and the amino moiety of 3-amino-1-propanol (**2**) (pathway a). This is followed by dehydrogenation of the alcoholic moiety of intermediate **4** by ruthenium catalyst to produce an aldehyde intermediate which can react with **1** to give an imine. And then, the imine is hydrogenated by ruthenium hydride generated by the initial dehydrogenation of intermediate **4** to give *N,N'*-diphenyl-1,3-diaminopropane (**6**). An alternative pathway is the initial formation of *N*-phenyl-1,3-diaminopropane (**5**) by similar sequence (dehydrogenation, condensation and reduction) between **1** and the alcoholic moiety of 3-amino-1-propanol (**2**) as described above (pathway b), which then reacts with aniline (**1**) through the amine exchange reaction to produce the intermediate **6**. Intermediate **6** formed from

Table 2

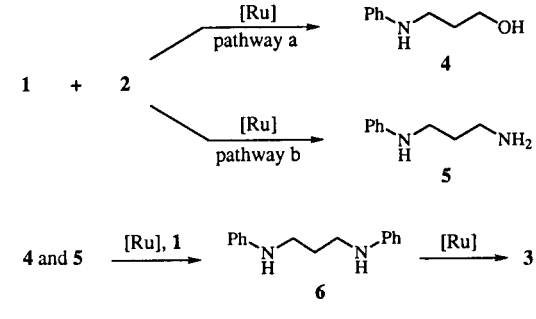
Ruthenium-Catalyzed Synthesis of Quinolines from Anilines and 3-Amino-1-propanol (2)[a]

Anilines	Quinolines	Yield [b]
aniline	quinoline	37
p-toluidine	6-methylquinoline	35
m-toluidine	5- and 7-methylquinoline	45 [c]
o-toluidine	8-methylquinoline	40
p-anisidine	6-methoxyquinoline	35
p-chloroaniline	6-chloroquinoline	29
p-butylaniline	6-butylaniline	42
p-*sec*-butylaniline	6-*sec*-butylquinoline	41
2,3-dimethylaniline	7,8-dimethylquinoline	43
2,5-dimethylaniline	5,8-dimethylquinoline	40
3,5-dimethylaniline	5,7-dimethylquinoline	46

[a] All reactions were carried out with anilines (6 mmoles), 3-amino-1-propanol (2) (1 mmole), $RuCl_3$•nH_2O (n = 3, 0.04 mmole), PPh_3 (0.12 mmole), $SnCl_2$•$2H_2O$ (1 mmole) and acetone (5 mmoles) in dioxane (10 ml) at 180° for 20 hours. [b] Isolated yields based on 2. [c] 5-Methylquinoline:7-methylquinoline = 1:5.

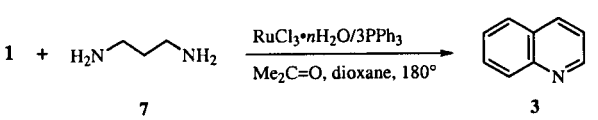
both pathway a and pathway b is followed by a similar catalytic cycle to that which has already been proposed in ruthenium-catalyzed synthesis of quinolines from anilines and 1,3-propanediol [16, 17].

Scheme 2



On the other hand, the following experimetal observation is worth noting as evidence for amine exchange reactions between aniline (**1**) and the amino moiety of 3-amino-1-propanol (**2**) as well as between aniline (**1**) and *N*-phenyl-1,3-diaminopropane (**5**) under the present ruthenium-catalyzed systems. In a separate experiment, we observed that a similar ruthenium-catalyzed heteroannulation between aniline (**1**) and 1,3-diaminopropane (**7**) resulted in the formation of quinoline (**3**) in 9% yield (Scheme 3).

Scheme 3



EXPERIMENTAL

^1H (400 MHz) and ^{13}C (100 MHz) nmr spectra were recorded on a Bruker Avance Digital 400 spectrometer using tetramethylsilane as an internal standard. Chemical shifts are reported in δ units downfield from tetramethylsilane. Electron impact mass spectra were obtained on a shimadzu QP-1000 spectrometer. Analyses (glc) were carried out with Shimadzu GC-17A equipped with CBP10-S25-050 column (Shimadzu, fused silica capillary column, 0.33 mm x 25 m, 0.25 μm film thickness) using nitrogen as the carrier gas. glc yields were determined using undecane as an internal standard. The isolation of pure products was carried out via column chromatography (silica gel 60 HF_{254}, Merck) and thin layer chromatography. Commercially available organic and inorganic compounds were used without further purification. Ruthenium catalysts such as dichlorotris(triphenylphosphine)-ruthenium(II) [25], Dodecacarbonyltriruthenium(0) [26] and Dihydridotetrakis(triphenylphosphine)ruthenium(II) [27] were prepared by the reported method.

General Procedure for Ruthenium-Catalyzed Synthesis of Quinolines.

A mixture of aniline (6 mmoles), 3-amino-1-propanol (1 mmole), ruthenium(III) chloride hydrate (10 mg, 0.04 mmole), triphenylphosphine (32 mg, 0.12 mmole), tin(II) chloride dihydrate (226 mg, 1 mmole), and acetone (0.37 ml, 5 mmoles) in dioxane (10 ml) was placed in a stainless steel pressure vessel. After the system was flushed with argon, the mixture was stirred at 180° for 20 hours. The reaction mixture was filtered through a short column (silica gel, chloroform-ethyl acetate mixture) to eliminate inorganic compounds and evaporated under reduced pressure. The residual oily material was separated by column chromatography (ethyl acetate-hexane) to give the starting aniline and the product quinoline. After subsequent treatment of the first separated mixture with an appropriate amount of acetic anhydride to convert aniline into *N*-acetylaniline (differentiation of polarity between aniline and quinoline), the mixture was separated by thin layer chromatography using ethyl acetate-hexane mixture as an eluent to give the corresponding pure quinolines. The products obtained by the above procedure were characterized spectroscopically as shown below. All products are known compounds.

6-Methylquinoline.

This compound was obtained as pale yellow oil; ^1H nmr (deuteriochloroform): δ 2.51 (s, 3H), 7.31 (dd, J = 4.2 and 8.0 Hz, 1H), 7.50-7.53 (m, 2H), 8.01 (t, J = 8.0 Hz, 2H), 8.83 (d, J = 3.2 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 21.5, 121.0, 126.6, 128.3, 129.1, 131.7, 135.3, 136.3, 146.9, 149.5.

5- and 7-Methylquinolines.

These compounds were isolated as a mixture and the molar ratio was determined from the peak areas of the clearly separated methyl protons in the ^1H nmr spectrum. 5-Methylquinoline. ^1H nmr (deuteriochloroform): δ 2.62 (s, 3H), 7.36 (d, J = 4.0 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 8.5 Hz, 1H), 8.89 (d, J = 4.0 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 18.5, 120.6, 127.0, 127.6, 127.7, 129.1, 132.3, 134.5, 149.9. 7-Methylquinoline. ^1H nmr (deuteriochloroform): δ 2.53 (s, 3H), 7.26 (dd, J = 4.0 and 8.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.88 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 8.84 (d, J = 4.0 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 21.8, 120.2, 126.3, 127.4, 128.4, 128.7, 135.6, 139.7, 148.5, 150.3.

8-Methylquinoline.

This compound was obtained as pale yellow oil; ^1H nmr (deuteriochloroform): δ 2.83 (s, 3H), 7.37-7.41 (m, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 6.8 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 8.13 (dd, J = 1.6 and 8.2 Hz, 1H), 8.95 (dd, J = 1.6 and 4.4 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 18.2, 120.8, 125.9, 126.3, 128.3, 129.6, 136.3, 137.1, 147.4, 149.3; ms: m/z (%) 143 (M^+, 100), 115 (17), 89 (6), 63 (4).

6-Methoxyquinoline.

This compound was obtained as pale yellow oil; ^1H nmr (deuteriochloroform): δ 3.91 (s, 3H), 7.05 (d, J = 2.4 Hz, 1H), 7.31-7.38 (m, 2H), 8.01 (t, J = 9.6 Hz, 2H), 8.76 (d, J = 2.8 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 55.5, 105.1, 121.3, 122.3, 129.3, 130.9, 134.8, 144.5, 147.9, 157.7.

6-Chloroquinoline.

This compound was obtained as pale yellow oil; ^1H nmr (deuteriochloroform): δ 7.42 (dd, J = 4.0 and 8.4 Hz, 1H), 7.65 (dd, J = 2.4 and 8.8 Hz, 1H), 7.80 (d, J = 2.4 Hz, 1H), 8.06 (t, J = 8.8 Hz, 2H), 8.91 (dd, J = 1.6 and 4.4 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 121.9, 126.4, 128.9, 130.4, 131.1, 132.3, 135.1, 146.7, 150.6.

6-Butylquinoline.

This compound was obtained as pale yellow oil; ^1H nmr (deuteriochloroform): δ 0.95 (t, J = 7.6 Hz, 3H), 1.32-1.42 (m, 2H), 1.65-1.72 (m, 2H), 2.78 (t, J = 7.6 Hz, 2H), 7.33 (dd, J = 4.4 and 8.4 Hz, 1H), 7.54-7.56 (m, 2H), 8.01-8.07 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 13.9, 22.4, 33.4, 35.6, 121.0, 126.0, 128.3, 129.2, 131.1, 135.5, 141.3, 147.1, 149.5; ms: m/z (%) 185 (M^+, 44), 156 (9), 142 (100), 115 (8), 77 (3).

6-sec-Butylquinoline.

This compound was obtained as pale yellow oil; ^1H nmr (deuteriochloroform): δ 0.84 (t, J = 7.2 Hz, 3H), 1.32 (d, J = 6.8 Hz, 3H), 1.65-1.73 (m, 2H), 2.75-2.83 (m, 1H), 7.34 (dd, J = 4.2 and 8.0 Hz, 1H), 7.56-7.60 (m, 2H), 8.07 (t, J = 9.2 Hz, 2H), 8.85 (dd, J = 1.2 and 4.0 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 12.2, 21.8, 31.0, 41.7, 121.0, 124.9, 128.3, 129.2, 129.6, 135.8, 146.0, 147.2, 149.5; ms: m/z (%) 185 (M^+, 87), 170 (15), 156 (100), 142 (23), 128 (27), 102 (10), 77 (12).

7,8-Dimethylquinoline.

This compound was obtained as pale yellow oil; ^1H nmr (deuteriochloroform): δ 2.46 (s, 3H), 2.75 (s, 3H), 7.25 (dd, J = 4.2 and 8.4 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 8.00 (dd, J = 1.6 and 8.2 Hz, 1H), 8.89 (dd, J = 1.6 and 4.0 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 13.3, 20.7, 119.8, 124.8, 126.6, 129.4, 134.2, 136.1, 137.1, 147.3, 149.1; ms: m/z (%) 157 (M^+, 100), 142 (23), 128 (7), 77 (9).

5,8-Dimethylquinoline.

This compound was obtained as reddish brown oil; ^1H nmr (deuteriochloroform): δ 2.61 (s, 3H), 2.77 (s, 3H), 7.23 (d, J = 7.2 Hz, 1H), 7.38 (dd, J = 4.2 and 8.6 Hz, 1H), 7.42 (d, J = 7.2 Hz, 1H), 8.26 (dd, J = 1.2 and 8.4 Hz, 1H), 8.93 (dd, J = 1.6 and 4.0 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 18.2, 18.4, 120.4, 126.7, 127.6, 129.2, 132.2, 132.6, 134.9, 147.6, 148.7; ms: m/z (%) 157 (M^+, 100), 142 (30), 128 (7), 77 (8).

5,7-Dimethylquinoline.

This compound was obtained as pale yellow oil; 1H nmr (deuteriochloroform): δ 2.49 (s, 3H), 2.60 (s, 3H), 7.17 (s, 1H), 7.29 (dd, J = 4.0 and 8.5 Hz, 1H), 7.73 (s, 1H), 8.20 (d, J = 8.5 Hz, 1H), 8.84 (dd, J = 2.0 and 4.5 Hz, 1H); 13C nmr (deuteriochloroform): δ 18.4, 21.8, 119.9, 125.7, 126.6, 129.3, 132.1, 134.1, 139.2, 148.9, 149.9; ms: m/z (%) 157 (M+, 100), 142 (44), 128 (7), 77 (5).

Ruthenium-Catalyzed Heteroannulation of Aniline (**1**) with 1,3-Diaminopropane (**7**).

A mixture of aniline (599 mg, 6 mmoles), 1,3-diaminopropane (74 mg, 1 mmole), ruthenium(III) chloride dihydrate (13 mg, 0.05 mmole), tin(II) chloride dihydrate (226 mg, 1 mmole), triphenylphosphine (39 mg, 0.15 mmole) and acetone (0.37 ml, 5 mmoles) in dioxane (10 ml) was placed in a stainless steel autoclave. After the system was flushed with argon, the mixture was stirred at 180° for 20 hours. The reaction mixture was filtered through a short column (silica gel, chloroform-ethyl acetate mixture) to eliminate inorganic compounds. To the filtrate was added undecane as an internal standard and the mixture was analyzed by gas chromatography.

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