The Ruthenium Complex Catalyzed *N*-Heterocyclization of Aminoarenes to Quinoline Derivatives Using Allylic Alcohols and Aliphatic Aldehydes[1)]

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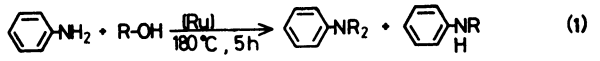
Aminoarenes reacted with 2-propen-1-ol and 2-buten-1-ol at 180 °C to give quinoline derivatives in fairly good yields in the presence of a catalytic amount of a ruthenium complex. Dichlorotris(triphenylphosphine)-ruthenium was the most effective catalyst. The aminoarenes with electron-releasing groups favored the formation of the quinolines. The *N*-heterocyclization also proceeded when aliphatic aldehydes were used in place of the allylic alcohols. The employment of allylic alcohols gave, however, higher yields in several cases. The reaction involves the isomerization of the allylic alcohols to the corresponding aldehydes. The aldehydes reacted with aminoarenes to give Schiff-base dimers which were then cyclized in the presence of the ruthenium complex to the quinolines. As a key intermediate in the reaction, the ortho-metallated species has been proposed.

Several methods have been reported using transition-metal complex catalysts for the formation of nitrogen heterocycles, such as pyrrole,[2)] indole,[3,4)] and quinoline[5,6)] derivatives. These procedures have been used to develop novel synthetic methods under non-acidic conditions.

In previous papers, we have demonstrated that rhodium, ruthenium, and palladium complexes were effective catalysts for the preparation of quinoline derivatives from aminoarenes and nitroarenes.[7-9a)] Aminoarenes were converted into quinoline derivatives in the presence of μ,μ'-dichlorobis(norbornadiene)-dirhodium(I) ($[RhCl(nbd)]_2$) by the reaction with aliphatic aldehydes.[7)] Nitroarenes were reductively converted into quinolines and (dialkylamino)arenes using aliphatic aldehydes in the presence of a rhodium–palladium binary catalyst system under carbon monoxide pressure.[8)] The quinoline derivatives were also obtained by the reductive transformation of nitroarenes using aliphatic alcohols in the presence of dichlorotris-(triphenylphosphine)ruthenium ($RuCl_2(PPh_3)_3$).[9a)] Recently, this nitroarene–aliphatic alcohol system was also adopted for the synthesis of the quinoline derivatives using a rhodium–molybdenum binary catalyst in a much larger amount (total 20 mol%).[9b)] These procedures provide a variety of synthetic methods for building up a quinoline nucleus.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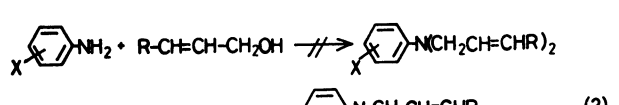
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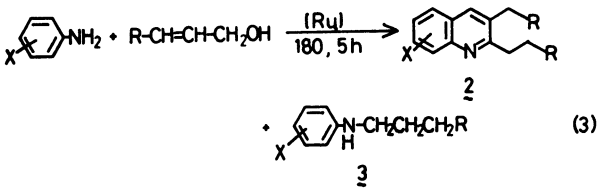
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Recently, we have revealed that aniline was effectively *N*-alkylated with a primary alcohol in the presence of a ruthenium catalyst (Eq. 1).[1)] When allylic alcohols were employed in place of the primary alcohol, we first expected that *N*-alkenylated products would be obtained in the same manner as when the saturated alcohols were employed (Eq. 2). However, that was not the case. Instead, quinoline derivatives and *N*-(alkylamino)-arenes were obtained as products, and no *N*-alkenylated products were formed.

This paper deals with the ruthenium-catalyzed synthesis of the quinoline derivatives by the *N*-heterocyclization of aminoarenes using allylic alcohols. The *N*-heterocyclization also proceeds with aliphatic aldehydes in place of allylic alcohols. The results with aliphatic aldehydes are also described.

Results and Discussion

Aminoarenes reacted with allylic alcohols, such as 2-propen-1-ol and 2-buten-1-ol, at 180 °C in the presence of a catalytic amount of ruthenium and rhodium complexes to give 2,3-dialkylquinolines and *N*-alkyl-aminoarenes in good yields (Eq. 3, Table 1).

When 2-buten-1-ol was employed (Runs 1—8), the yield of 3-ethyl-2-propylquinoline depended greatly on the catalyst used. The highest yield was achieved with $RuCl_2(PPh_3)_3$ (Run 1). Ruthenium trichloride was also active, but the quinoline was obtained in a lower yield (Run 2). However, ruthenium complexes, such as $RuH_2(PPh_3)_4$, $RuHCl(PPh_3)_3$, $RuHCl(CO)(PPh_3)_3$, and $Ru(CO)_3(PPh_3)_2$, had almost no catalytic activity for the *N*-heterocyclization (Runs 3—6). On the other hand, $[RhCl(nbd)]_2$, which was the most effective catalyst for the *N*-heterocyclization of aminoarenes with *aldehydes*,[7)] showed only a low catalytic activity for this reaction (Run 7). The *N*-heterocyclization did not proceed at all without the catalyst (Run 8).

A similar trend was observed when 2-propen-1-ol was employed (Runs 9—12), although the best yield of 2-ethyl-3-methylquinoline was realized with ruthenium trichloride as a catalyst (Run 10). $RuHCl(CO)(PPh_3)_3$ had some activity (Run 11). $[RhCl(nbd)]_2$ showed also a low activity for the *N*-heterocyclization (Run 12).

The effects of other reaction variables were also

Table 1. Preparation of quinoline derivatives from aniline and allylic alcohols using ruthenium and rhodium complexes[a]

Run	Alcohol	Catalyst	Conversion/%[b]	Yield/%[b]	
				2[c]	3[c]
1	2-Buten-1-ol	$RuCl_2(PPh_3)_3$	100	54	27
2	2-Buten-1-ol	$RuCl_3 \cdot nH_2O$	96	22	22
3	2-Buten-1-ol	$RuH_2(PPh_3)_4$	77	0	Trace
4	2-Buten-1-ol	$RuHCl(PPh_3)_3$	74	Trace	Trace
5	2-Buten-1-ol	$RuHCl(CO)(PPh_3)_3$	87	Trace	Trace
6	2-Buten-1-ol	$Ru(CO)_3(PPh_3)_2$	66	0	Trace
7	2-Buten-1-ol	$[RhCl(nbd)]_2$	85	18	21
8	2-Buten-1-ol	None	0	0	0
9	2-Propen-1-ol	$RuCl_2(PPh_3)_3$	98	42	2
10	2-Propen-1-ol	$RuCl_3 \cdot nH_2O$	100	43	2
11	2-Propen-1-ol	$RuHCl(CO)(PPh_3)_3$	85	11	2
12	2-Propen-1-ol	$[RhCl(nbd)]_2$	100	29	14

a) A mixture of aniline (20 mmol), alcohol (10 ml), a catalyst (0.2 mmol, 1.0 mol% based on aniline charged), and nitrobenzene (22 mmol) was stirred at 180 °C for 5 h. b) Determined by GLC based on aniline charged. c) See Eq. 3.

Table 2. Preparation of quinoline derivatives from aniline and allylic alcohols under various reaction conditions[a]

Run	Alcohol	Catalyst[b] (mol%)	Conversion/%[b]	Yield/%[b]	
				2[c]	3[c]
1	2-Buten-1-ol	1.0	≈100	54	27
13[d]	2-Buten-1-ol	1.0	78	31	8
14	2-Buten-1-ol	0.5	65	16	Trace
15	2-Buten-1-ol	2.0	≈100	51	22
16[e]	2-Buten-1-ol	1.0	≈100	45	17
17[f]	2-Buten-1-ol	1.0	87	63	13
18[e]	2-Propen-1-ol	1.0	≈100	33	4
19[f]	2-Propen-1-ol	1.0	89	49	2

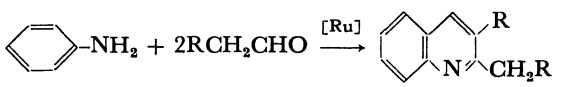
a) A mixture of aniline (20 mmol), alcohol (10 ml), $RuCl_2(PPh_3)_3$, and nitrobenzene (22 mmol) was stirred at 180 °C for 5 h. b) Based on aniline charged. c) See Eq. 3. d) Reaction temp; 150 °C. e) Without nitrobenzene. f) Benezene (10 ml) was added to the reaction mixture.

Table 3. Preparation of quinoline derivatives from aniline and aldehydes[a]

Run	Aldehyde	Conversion/%[b]	Yield/%[b]	
			2[c]	3[c]
20	Pentanal	≈100	(33)[d]	—
21	Butanal	99	59	29
22	Butanal[e]	92	55	35
23	Propanal	≈100	58	16
24	Propanal[e]	98	51	8

a) A mixture of aniline (20 mmol), aldehyde (10 ml; 94—138 mmol), $RuCl_2(PPh_3)_3$(0.2 mmol), and nitrobenzene (20 mmol) was stirred at 180 °C for 5 h. b) Based on aniline charged by GLC. c) See Eq. 3. d) Isolated yield. e) A mixture of aniline (20 mmol), aldehyde (44 mmol; 1.6—2.3 ml), benzene (10 ml), $RuCl_2(PPh_3)_3$ (0.2 mmol), and nitrobenzene (22 mmol) was stirred at 180 °C for 5 h.

examined; the results are shown in Table 2. A lower reaction temperature (150 °C) and a smaller amount of the catalyst (0.5 mol%) resulted in decreases in the conversion of aniline and in the yield of the quinoline (Runs 13 and 14). However, the yield was not improved by increasing the amount of the catalyst to 2.0 mol% (Run 15). These results indicate that an elevated temperature (180 °C) is required and that a 1.0 mol% catalyst is sufficient for a moderate yield of the quinoline. The yields of the quinolines decreased in the absence of nitrobenzene, which is considered to operate as an oxidant in the dehydrogenation step from hydroquinoline to the quinoline derivative (*vide infra*) (Runs 16 and 18). The dilution of the reaction system with benzene improved the yield of the quinoline derivatives (Runs 17 and 19).



(4)

The allylic alcohols can be replaced by aliphatic aldehydes (Eq. 4). The results are listed in Table 3. Employing pentanal in excess, 2-butyl-3-propylquinoline was obtained in a 33% isolated yield (Run 20). Butanal and propanal also gave the corresponding quinolines (Runs 21 and 23). On the other hand, in the rhodium-catalyzed preparation of quinolines using aldehydes,[8]

TABLE 4. PREPARATION OF QUINOLINE DERIVATIVES FROM AMINOARENES AND ALLYLIC ALCOHOLS OR ALDEHYDE[a]

Run	Aminoarene Nitroarene (X=)	Allylic alcohol or aldehyde	Product (Yield/%)[b]
25	*p*-MeO	2-Buten-1-ol	3-Ethyl-6-methoxy-2-propylquinoline (81) *N*-Butyl-*p*-anisidine (8)
26[c]	*p*-MeO	2-Buten-1-ol	3-Ethyl-6-methoxy-2-propylquinoline (83) *N*-Butyl-*p*-anisidine (8)
27[d]	*p*-MeO	2-Buten-1-ol	3-Ethyl-6-methoxy-2-propylquinoline (63) *N*-Butyl-*p*-anisidine (17)
28	*p*-MeO	Butanal	3-Ethyl-6-methoxy-2-propylquinoline (69) *N*-Butyl-*p*-anisidine (13)
29	*p*-Me	2-Buten-1-ol	3-Ethyl-6-methyl-2-propylquinoline (82) *N*-Butyl-*p*-toluidine (36)
30[c]	*p*-Me	2-Buten-1-ol	3-Ethyl-6-methyl-2-propylquinoline (97) *N*-Butyl-*p*-toluidine (36)
31[d]	*p*-Me	2-Buten-1-ol	3-Ethyl-6-methyl-2-propylquinoline (73) *N*-Butyl-*p*-toluidine (35)
32	*p*-Me	Butanal	3-Ethyl-6-methyl-2-propylquinoline (64) *N*-Butyl-*p*-toluidine (47)
33	*p*-Cl	2-Buten-1-ol	6-chloro-3-ethyl-2-propylquinoline (17)
34	*p*-MeO	2-Propen-1-ol	2-Ethyl-6-methoxy-3-methylquinoline (56)
35	*p*-Me	2-Propen -1-ol	2-Ehtyl-6, 3-dimethylquinoline (61)
36	*o*-MeO	2-Buten-1-ol	3-Ethyl-8-methoxy-2-propylquinoline (15)
37	*o*-Me	2-Buten-1-ol	3-Ethyl-8-methyl-2-propylquinoline (23)
38	*o*-Cl	2-Buten-1-ol	8-Chloro-3-ethyl-2-propylquinoline (Trace)

a) A mixture of aminoarene (20 mmol), nitroarene (22 mmol), allylic alcohol or aldehyde (10 ml), benzene (10 ml), and $RuCl_2(PPh_3)_3$ (0.2 mmol) was stirred at 180 °C for 5 h. b) Determined by GLC based on aminoarene charged. c) Reaction time was 7.5 h. d) The reaction was carried out without nitroarene.

an excess of aliphatic aldehyde interfered with the formation of the quinolines because of side reactions, *e.g.*, aldol condensation. In the present reaction, the employment of 2.2 equivalents of aldehyde did not affect the yield essentially (Runs 22 and 24). The present results indicate that the ruthenium catalyst can be used in the preparation of the quinolines from aniline and aliphatic aldehydes, though its catalytic activity is lower than that of the rhodium catalyst described in a previous paper.[7] However, the rhodium catalyst was revealed to be less effective for the preparation of quinolines with allylic alcohols, as has been mentioned above.

This procedure is applicable to a variety of aminoarenes for the preparation of various substituted quinolines. The results for para- and ortho-substituted anilines with methyl, methoxyl, and chloro substituents are summarized in Table 4. 3-Ethyl-6-methoxy-2-propylquinoline was produced in an 81% yield by the reaction of *p*-anisidine with 2-buten-1-ol (Run 25). Prolonging the reaction time slightly improved the yield (Run 26), while the absence of the nitroarene (*p*-nitroanisole) reduced the yield (Run 27). The use of butanal in place of 2-buten-1-ol resulted in a decrease in the yield of the substituted quinoline (Run 28). *p*-Toluidine and 2-buten-1-ol gave 3-ethyl-6-methyl-2-propylquinoline in an 82% yield (Run 29). Prolonging the reaction time appreciably improved the yield to 97% (Run 30). On the other hand, the absence of nitroarene (*p*-nitrotoluene) and the use of butanal in place of 2-buten-1-ol gave poorer yields of the substituted quinoline (Runs 31 and 32). 6-Chloro-3-ethyl-2-propylquinoline was also obtained, but in a poor yield (17%), when *p*-chloroaniline was employed as an aminoarene (Run 33).

The results obtained with *p*-substituted anilines clearly indicate that aminoarenes with electron-releasing groups, *i.e.*, aminoarenes with high pK_a values, favor the *N*-heterocyclization to quinoline derivatives. Furthermore, the employment of 2-buten-1-ol in place of butanal is more favorable to the *N*-heterocyclization.

2-Propen-1-ol reacted in a similar manner with *p*-anisidine and *p*-toluidine to give 2-ethyl-6-methoxy-3-methylquinoline and 2-ethyl-3,5-dimethylquinoline in moderate yields (Runs 34 and 35).

In contrast, ortho-substituted aminoarenes gave 8-substituted quinoline derivatives only in low yields (Runs 36—38). This is presumably the result of a steric effect of the ortho-substituting groups, which interfere with the coordination of the amino group to the ruthenium catalyst.

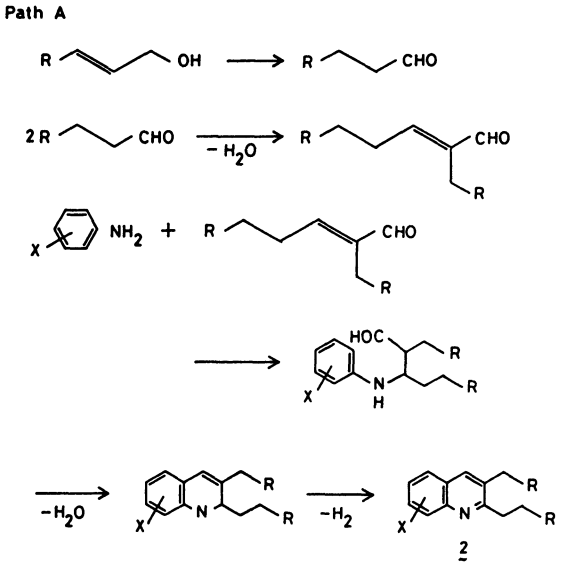
There have been several studies concerning the ruthenium- or rhodium-catalyzed isomerization of allylic alcohols to ketones and aldehydes.[10,11] The present reaction is believed to include the isomerization of the allylic alcohols to the corresponding aldehydes. Indeed, 2-buten-1-ol and 2-propen-1-ol were isomerized to butanal and propanal in 59 and 29% yields respectively in the presence of $RuCl_2(PPh_3)_3$ under conditions similar to those for the *N*-heterocyclization (Eq. 5; see Experimental section). In the present *N*-heterocyclization, the aldehydes produced are considered to react with

$$RCH{=}CHCH_2OH \xrightarrow[180\,^\circ C,\ 5\,h]{RuCl_2(PPh_3)_3} RCH_2CH_2CHO \qquad (5)$$

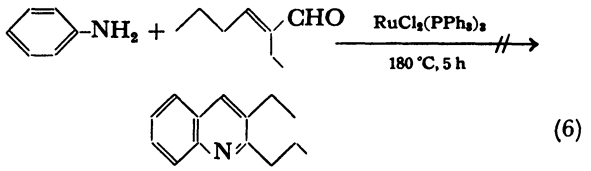
	Yield/%
$R=CH_3$	59
$R=H$	29

aminoarenes to give the quinoline derivatives.

In this reaction *N*-alkylaminoarenes as well as the quinoline derivatives were formed. Saturated alcohols were obtained in the isomerization reaction of the allylic alcohols (see Experimental section). Therefore, we can safely say that the saturated alcohols functioned as *N*-alkylating reagents in the reaction, as has previously been reported (Eq. 1).[1] The saturated alcohols can be produced by the hydrogenation of the allylic alcohols, since $RuCl_2(PPh_3)_3$ is known to be an effective catalyst for the hydrogen-transfer reaction from alcohols.[12]

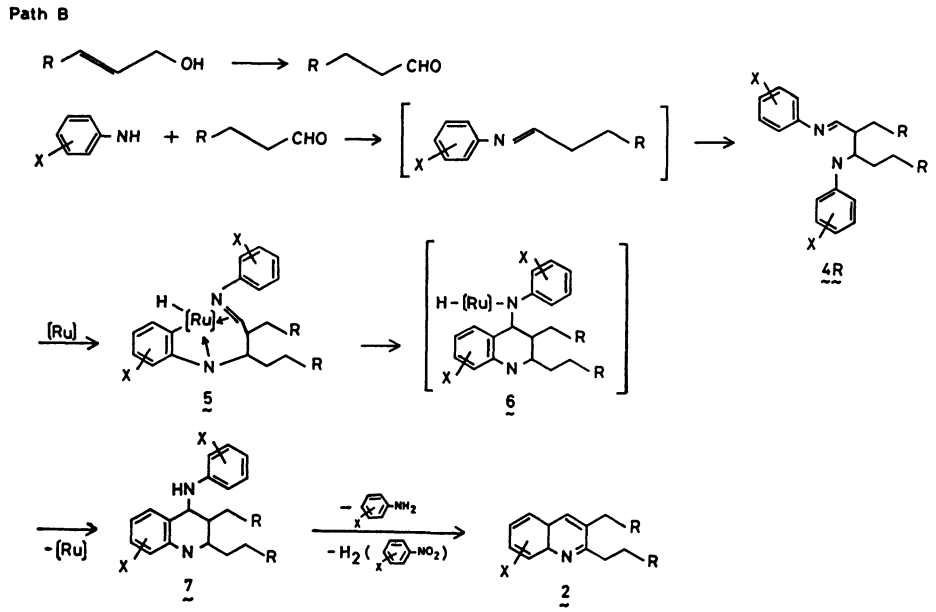


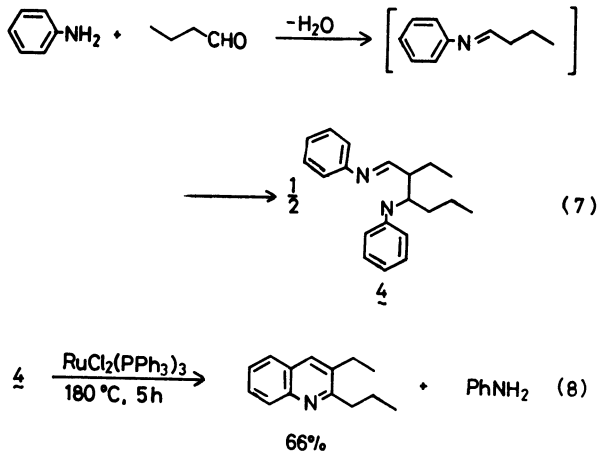
Some further studies on the mechanism of the *N*-heterocyclization to the quinolines have been carried out. Two reaction pathways are considered for the reaction. One is the path *via* aldol condensation, followed by the Michael-type addition of aminoarene (Path A). Transition metal-catalyzed aldol condensation reactions have been reported by several authors.[13] In order to examine the possibility of Path A, aniline was reacted with 2-ethyl-2-hexenal, which is an aldol condensate of butanal obtained by the method of the literature.[14] However, the corresponding quinoline, 3-ethyl-2-propylquinoline, was not obtained at all by the reaction (Eq. 6). Therefore, Path A seems not to be probable.



(6)

Aniline is known to react with an aldehyde to give a Schiff-base dimer.[15] The second pathway to the quinolines is one *via* the Schiff-base dimer (Path B). An equimolar mixture of aniline and butanal readily gave a Schiff-base dimer (**4**) at room temperature as white crystals (60% yield, lit, 78% yield[15b]) (Eq. 7). This Schiff-base dimer (**4**) was effectively converted to 3-ethyl-2-propylquinoline in the presence of $RuCl_2$-$(PPh_3)_3$ (Eq. 8). Without the ruthenium complex or with 1 mol% (based on **4**) $ZnCl_2$, the corresponding quinoline was not obtained under the same reaction conditions. These results strongly suggest that the *N*-heterocyclization proceeds *via* the Schiff-base dimer and that the ruthenium catalyst operates in the cyclization stage. In Path B, the Schiff-base dimer, **4R**, forms presumably without the assistance of the ruthenium catalyst. Several transition metals have been reported to activate the aromatic *ortho*-C–H bond by oxidative addition to that bond, that is, by so-called orthometallation.[16] The ligands containing nitrogen are good ligands for maintaining such ortho-metallated species.[17] Furthermore, ruthenium is one of the most active central transition metals generating the ortho-metallated species.[18] Therefore, as one of the most plausible mechanisms of the cyclization stage, we propose the





one *via* ortho-metallated species, such as **5**. This reaction is considered to proceed from **5** to **6** by an insertion of the C=N bond into the Ru–C bond.[19] The following reductive elimination of active ruthenium species will generate **7**. Finally, the quinoline is obtained by the elimination of aniline and hydrogen from **7**. The elimination of hydrogen is favored by the presence of nitroarene.

In this study, aminoarene with an electron-releasing group favored the formation of the quinoline derivatives. This might be because the more basic aminoarene facilitates a nucleophilic attack on the carbonyl carbon of the aldehyde, and so favors the formation of the Schiff-base dimer.

Experimental

Materials and Catalysts. The alcohols, aldehydes, aminoarenes, and nitroarenes were commercial products and were purified by distillation or crystallization before use. The $RuCl_3 \cdot nH_2O$ (mainly trihydrate) was purchased from Wako Chemicals and was used without further purification. The $RuCl_2(PPh_3)_3$,[21] $RuH_2(PPh_3)_4$,[22] $RuHCl(PPh_3)_3$,[23] $RuHCl(CO)(PPh_3)_3$,[24] $Ru(CO)_3(PPh_3)_2$,[25] and $[RhCl(nbd)]_2$[25] were prepared according to the methods in the literatures.

Reaction Procedure and Identification of the Products. A mixture of aminoarene (20 mmol), allylic alcohol or aliphatic aldehyde (10 ml), a ruthenium catalyst (0.20 mmol, 1.0 mol% based on aminoarene charged), nitroarene (22 mmol), and benzene (10 ml), if required, was placed in a glass liner. The glass liner was set in a 50 ml stainless steel autoclave (Taiatsu Kogyo) and the mixture was stirred with a magnetic stirrer at 180 °C for 5 h under an argon atmosphere. The GLC analysis of the reaction mixture was performed with 5% Apiezon Grease L supported on Neopak 1A 60—80 mesh (0.3 cmϕ × 3 m) by the internal-standard method. The product was isolated by fractional distillation or by medium-pressure column chromatography (silica gel, Merck No. 9385, as the absorbent and hexane–ethyl acetate as the eluent) and identified by means of ^{1}H-, ^{13}C-NMR, IR, mass spectra, and elemental analysis.

Identification of the Products. The ^{1}H-NMR spectra were obtained with a Varian HR-220(220 MHz) or JEOL JNM FX100 (100 MHz) spectrometer. The ^{13}C NMR spectra were recorded at 25.05 MHz on a JEOL JNM FX100 spectrometer. The IR spectra were measured on a Hitachi model 215 grating spectrometer, and the mass spectra were recorded on a JMS 01SG mass spectrometer. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

N-*Butyl*-p-*toluidine.* ^{1}H-NMR ($CDCl_3$) δ=0.94 (t, 3H), 1.48 (m, 4H), 2.21 (s, 3H), 3.02 (t, 2H), 3.35 (s, 1H), 6.47—7.04 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ=13.9(s), 20.4(s), 20.4(s), 31.8(s), 44.1(s), 112.9(s), 126.1(s), 129.6(s), 146.3(s); IR 3400 cm^{-1} (ν NH).

N-*Butyl*-p-*anisidine.* ^{1}H-NMR ($CDCl_3$) δ=0.92 (t, 3H), 1.36 (m, 2H), 1.51 (m, 2H), 2.98 (t, 2H), 3.27 (s, 1H), 3.66 (s, 3H), 6.47—6.77 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ= 14.0(s), 20.4(s), 31.8(s), 44.6(s), 55.7(s), 113.9(s), 114.9(s), 142.9(s), 151.8(s); IR 3400 cm^{-1} (ν NH). The spectral data of the other products which appeared in this study were all consistent with those reported in the previous paper.[7]

Isomerization of Allylic Alcohols. In a glass liner, 2-propen-1-ol (5.0 ml, 74.6 mmol) and $RuCl_2(PPh_3)_3$ (95.9 mg, 0.10 mmol) were placed. The glass liner was then set in the autoclave, and the mixture was stirred with magnetic stirrer at 180 °C for 5 h under an argon atmosphere. The subsequent GLC analysis of the reaction mixture showed that 96% of the 2-propen-1-ol was converted and that 22 mmol (29% based on the 2-propen-1-ol used) of propanal and 7.5 mmol (10%) of propanol were obtained.

The isomerization of 2-buten-1-ol (5.0 ml, 60.5 mmol) with $RuCl_2(PPh_3)_3$ (95.9 mg, 0.10 mmol) was carried out in a similar manner. The conversion of 2-buten-1-ol was almost 100%, and 36 mmol (59% based on 2-buten-1-ol used) of butanal and 9.7 mmol (16%) of butanol) were formed.

Reaction of Aniline with 2-Ethyl-2-hexenal. A mixture of aniline (11 mmol), 2-ethyl-2-hexenal (15 mmol), nitrobenzene (12 mmol), benzene (5.0 ml), and $RuCl_2(PPh_3)_3$ (0.10 mmol) was stirred at 180 °C for 5 h under an argon atmosphere. The GLC analysis of the reaction mixture showed that no 3-ethyl-2-propylquinoline was obtained, although considerably aniline was converted.

Transformation of **4** *into 3-Ethyl-2-propylquinoline.* A solution of **4** (2.94 g, 10 mmol) in benzene (20 ml) was stirred in the presence of nitrobenzene (20 mmol) and $RuCl_2(PPh_3)_3$ (0.20 mmol) at 180 °C for 5 h. After the reaction mixture had cooled, 6.6 mmol (66% yield based on **4**) of 3-ethyl-2-propylquinoline was found by GLC analysis. When the reaction was carried out in the absence of nitrobenzene, the yield of the quinoline decreased to 3.4 mmol (34% yield).

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