Ruthenium-Catalyzed N-Alkylation and N-Benzylation of Aminoarenes with Alcohols

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Aminoarenes were readily converted into secondary and tertiary amines by the reaction at 150–180 °C with primary alcohols in the presence of a catalytic amount (1 mol % based on the aminoarene) of a ruthenium complex. Dichlorotris(triphenylphosphine)ruthenium was the most effective catalyst precursor. Secondary amines were obtained in excellent yields when aminoarenes reacted with an equimolar amount of alcohols. With excess alcohols, tertiary amines were obtained predominantly. Kinetic measurements revealed that the rate had zero-order dependence on aminoarene concentration and first-order dependence on alcohol concentration and initial concentration of the ruthenium catalyst. From the kinetic features, the possible catalytic cycle, which includes the nucleophilic attack of the aminoarene on aldehyde intermediate, was postulated.

Introduction

Several methods using alkyl halides have been developed for the N-alkylation of amines.[1,2] However, these procedures are not usually feasible methods for the preparation of primary or secondary amines. Therefore, various other reagents have been explored and in many cases offer practical advantages. These reagents include methyl trifluoromethanesulfonate,[3] methyl sulfite,[4] and phosphonium salts derived from alcohols.[5]

On the other hand, much attention has been focused on reductive N-alkylation,[6-8] where aldehydes or ketones react with amine in the presence of hydrogen and a catalyst to yield N-alkylated amines. We have reported the reductive N-alkylation of amines with aldehydes employing potassium tetracarbonylhydridoferrate as a reductant under mild conditions.[9]

Recently, several papers briefly reported the N-alkylations of amines employing alcohols as the alkylating reagents.[10-13] However, only few of the examples reported show synthetic value and little is known about the mechanism of the system. In this paper, we described a detailed investigation of the N-alkylation and N-benzylation of aminoarenes with alcohols (eq 1), including kinetic measurements and mechanistic studies on the ruthenium(II) catalysis system.

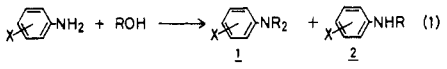

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Table I. The Ruthenium-Catalyzed N-Alkylation and N-Benzylation of Aniline with Various Alcohols[a]

run	alcohol	convn,[b] %	product[c] R	yield,[b,c] % 1	2
1	ethanol	100	Et	74	13
2	1-propanol	100	*n*-Pr	88	10
3	1-butanol	100	*n*-Bu	79	15
4	benzyl alcohol	100	$PhCH_2$	60	22
5	methanol[d]	59	Me	1	12
6	2-propanol	31	*i*-Pr	0	25
7	2-butanol	29	*sec*-Bu	0	28

[a] Aniline (40 mmol), alcohol (20 mL, [alcohol]/[aniline] = 4.8–12.3), $RuCl_2(PPh_3)_3$ (0.40 mmol, 1 mol% based on aniline charged) at 180 °C for 5 h. [b] Based on aniline charged, by GLC. [c] See eq 1. X = H. [d] $RuCl_2(PPh_3)_3$ (0.80 mmol).

Results

Reaction with Various Alcohols. Several alcohols were examined for their ability as N-alkylating or N-benzylating reagents in the presence of $RuCl_2(PPh_3)_3$ as the catalyst (Table I). Aniline was employed as aminoarene. With ethanol, 1-butanol, and benzyl alcohol in excess, the reactions proceeded smoothly to give *N,N*-disubstituted aniline in good yield (runs 1–4). The N-monosubstituted aniline were also obtained as a minor product. These results indicate that those alcohols function as good N-alkylating and N-benzylating reagents in the presence of the ruthenium catalyst. However, methanol showed only low reactivity for this reaction to give *N*-methylaniline in poor yield even with 2.0 mol % catalyst (run 5). When secondary alcohols, such as 2-propanol and 2-butanol, were employed, the conversions of aniline were low and only the N-monoalkylated anilines were obtained in low yields (runs 6 and 7). Thus, for the present reaction, primary alcohols other than methanol are effective.

Activities of Various Catalyst Precursors. The reactions were carried out in the presence of various ruthenium and rhodium complexes (Table II). With 0.5 mol % $RuCl_2(PPh_3)_3$, the reaction was slow and the yields of *N,N*-diethylaniline increased with longer reaction time (runs 8–10). In the presence of 1.0 mol % $RuCl_2(PPh_3)_3$, the reaction proceeded faster (run 1). Carbonylchlorohydridotris(triphenylphosphine)ruthenium ($RuHCl(CO)(PPh_3)_3$) (run 11) had some activity, but the reaction stopped predominantly at the monoalkylation stage. Murahashi and co-workers have reported that dihydridotetrakis(triphenylphosphine)ruthenium ($RuH_2(PPh_3)_4$) is active for the transformation of aliphatic amine into secondary and tertiary amines with alcohols.[11] However, for

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Table II. The Ruthenium-Catalyzed N-Alkylation of Aniline with Various Ruthenium Catalysts[a]

run	catalyst	alcohol	convn,[b] %	product[h] R	yield,[b] % 1	2
8	$RuCl_2(PPh_3)_3$[c,d]	ethanol	60	Et	7	53
9	$RuCl_2(PPh_3)_3$[c,d]	ethanol	100	Et	37	54
10	$RuCl_2(PPh_3)_3$[c,e]	ethanol	100	Et	69	4
1	$RuCl_2(PPh_3)_3$	ethanol	100	Et	74	13
11	$RuHCl(CO)(PPh_3)_3$	1-propanol	100	*n*-Pr	12	65
12	$RuH_2(PPh_3)_4$	ethanol	23	Et	0	6
13	$RuH_2(PPh_3)_4$	1-propanol	94	*n*-Pr	0	9
14	$Ru(CO)_3(PPh_3)_2$	1-propanol	1	*n*-Pr	0	t[g]
15	$RuCl_3 \cdot nH_2O$	1-propanol	0		0	0
16	$RhH(PPh_3)_4$	1-butanol	1	*n*-Bu	0	t[g]
17	$RhCl(PPh_3)_3$	1-butanol	0		0	0
18	none[f]	ethanol	0		0	0

[a] Aniline (40 mmol), alcohol (20 mL; [alcohol]/[aniline] = 5.5–8.6), catalyst (0.40 mmol, 1 mol% based on aniline) at 180 °C for 5 h. [b] Based on aniline charged, by GLC. [c] Catalyst (0.20 mmol, 0.5 mol% based on aniline). [d] Catalyst (0.20 mmol) for 10 h. [e] Catalyst (0.20 mmol) for 17 h. [f] Without the catalyst. [g] t = trace. [h] See eq 1. X = H.

Table III. N-Alkylation of Various Aminoarenes with Alcohols[a]

run	aminoarene	alcohol	temp, °C	time, h	product[b] X	R	yield,[c] % 1	2
19	4-methoxybenzenamine	1-butanol	180	5	4-OMe	*n*-Bu	91	7
20	4-methoxybenzenamine	benzyl alcohol	150	3	4-OMe	$PhCH_2$	83	17
21	4-methylbenzenamine	1-butanol	180	5	4-Me	*n*-Bu	85	15
22	4-methylbenzenamine	benzyl alcohol	150	3	4-Me	$PhCH_2$	77	23
23	4-chlorobenzenamine	benzyl alcohol	150	3	4-Cl	$PhCH_2$	46	53
24	2-methoxybenzenamine	1-butanol	180	5	2-OMe	*n*-Bu	33	63
25	*N*-ethylbenzenamine	1-octanol	180	5	*d*		86	

[a] Aminoarene (40 mmol), alcohol (20 mL), $RuCl_2(PPh_3)_3$ (0.40 mmol). [b] See eq 1. [c] Based on aminoarene charged, by GLC. [d] *N*-Ethyl-*N*-octylbenzenamine.

Table IV. N-Monoalkylation and N-Monobenzylation of Various Aminoarenes with Alcohols[a,b]

run	aminoarene	alcohol	temp, °C	time, h	product[c] X	R	yield,[d] % 2	1
26	benzenamine	1-butanol	180	5	H	*n*-Bu	79	6
27	benzenamine	benzyl alcohol	150	2	H	$PhCH_2$	100	0
28	4-methoxybenzenamine	1-butanol	180	5	4-OMe	*n*-Bu	99 (75)[e]	t[f]
29	4-methoxybenzenamine	benzyl alcohol	150	1.5	4-OMe	$PhCH_2$	100	0
30	4-methylbenzenamine	1-butanol	180	5	4-Me	*n*-Bu	99	t[f]
31	4-methylbenzenamine	benzyl alcohol	150	1.5	4-Me	$PhCH_2$	100	0
32	4-chlorobenzenamine	1-butanol	150	7	4-Cl	*n*-Bu	99 (82)[e]	t[f]
33	4-chlorobenzenamine	benzyl alcohol	150	4	4-Cl	$PhCH_2$	100	0

[a] Aminoarene (40 mmol), alcohol (40 mmol; 1-butanol 3.7 mL, benzyl alcohol 4.1 mL), $RuCl_2(PPh_3)_3$ (0.40 mmol). [b] 1,2,3,4-Tetrahydronaphthalene (10 mL) was employed as solvent when benzyl alcohol was used. [c] See eq 1. [d] Based on the aminoarene charged, by GLC. [e] Isolated yield. [f] t = trace.

the aminoarenes, $RuH_2(PPh_3)_4$ was ineffective as indicated by runs 12 and 13. Tricarbonylbis(triphenylphosphine)-ruthenium ($Ru(CO)_3(PPh_3)_2$) and ruthenium(III) chloride had no catalytic activity for this reaction. Moreover, hydridotetrakis(triphenylphosphine)rhodium ($RhH(PPh_3)_4$) and chlorotris(triphenylphosphine)rhodium ($RhCl(PPh_3)_3$), which have been reported to be active for the N-alkylation of aliphatic amine with alcohols,[12] were inative for the aminoarene (runs 16 and 17). These results indicate that the active catalyst precursor for the N-alkylation of aminoarene is different from that for the N-alkylation of aliphatic amine. Practically only $RuCl_2(PPh_3)_3$ showed high catalytic activity for the N-alkylation of the aminoarene as far as we have examined. Without the catalyst the reaction did not proceed at all.

Table III shows the results obtained with varous aminoarenes as substrates. 1-Butanol or benzyl alcohol was used in excess. The results of 4-substituted benzenamines indicate that the introduction of electron-releasing substituents enhance the rate of the reaction and increase the yields of 1, whereas ortho substituents or electron-withdrawing substituents at the 4-position inhibited the reactions and led to considerable formation of 2. In this procedure, two different alkyl groups can be placed on the nitrogen atom by the reaction of the N-alkylaniline as exemplified by run 25. The alkyl exchange of amine[14-16] did not occur appreciably.

It is well-known that N-alkylation with alkyl halide is not regulated at the N-mono- or N,N-dialkylation stage, since alkylated products are stronger bases and the reaction becomes faster.[2] However, in the present reaction such a regulation can be achieved by controlling a molar ratio of alcohol to aminoarene. When an equimolar amount of alcohol is employed, (*N*-monoalkyl- or (*N*-monobenzylamino)arenes are obtained in excellent yields and in many cases in 100% yields (Table IV). Such a regulation seems to be quite important for selective organic synthesis.

Kinetic Measurements. The kinetic features of the reaction were investigated employing aniline and benzyl

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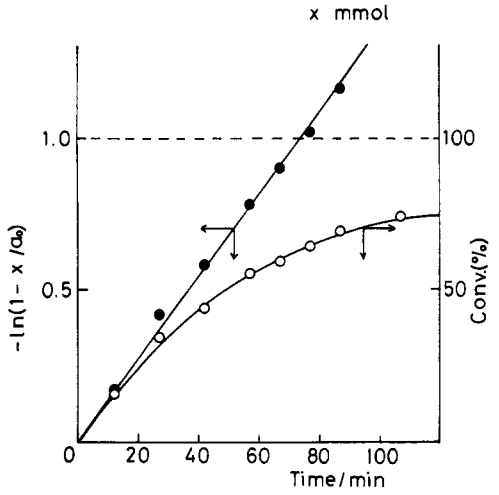

Figure 1. Determination of total order with respect to aminoarene and alcohol. Conversion (○), 1st plot (●): $[a]_0$ = $[\text{aniline}]_0$ = $[\text{benzyl alcohol}]_0$ = 1.54 mol dm^{-3}, $[RuCl_2(PPh_3)_3]_0$ = 1.54 × 10^{-2} mol dm^{-3}, 1,2,3,4-tetrahydronaphthalene (18.1 mL), [*o*-terphenyl] = 0.58 mol dm^{-3} as an internal standard at 180 °C.

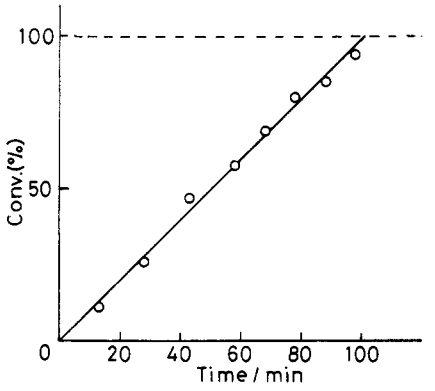

Figure 2. Zero-order dependence on aminoarene concentration. $[\text{Aniline}]_0$ = 0.31 mol dm^{-3}, $[\text{benzyl alcohol}]_0$ = 1.54 mol dm^{-3}, $[RuCl_2(PPh_3)_3]_0$ = 3.86 × 10^{-3} mol dm^{-3}, 1,2,3,4-tetrahydronaphthalene (21.1 mL), [*o*-terphenyl] = 0.59 mol dm^{-3} as an internal standard at 180 °C.

alcohol as the reactants. We employed benzyl alcohol because the reaction can be performed under reflux and the samplings are easy during the kinetics runs. Since benzyl alcohol behaves in a similar manner as other primary alcohols employed in this study (vide supra), it is safe to say that generalities of the reaction system will not suffer in the kinetic measurements. Furthermore, in order to simplify the kinetic treatment, the reaction was performed under the conditions where only N-monobenzylation took place. In the reactions discussed below, almost no N,N-disubstituted aniline was detected (less than 0.05%). First the reaction was carried out with an equimolar mixture of aniline and benzyl alcohol (each a_0 = 40 mmol). Plots of the $-\ln(1 - x/a_0)$ value vs. time show a linear relationship (Figure 1), where x is the amount (mmol) of *N*-benzylbenzenamine formed. This result indicates that the total order with respect to those two reactants is one.

Furthermore, with the amount of benzyl alcohol in large molar excess and held relatively constant, the rate was shown to be virtually constant throughout the reaction (Figure 2). This phenomenon clearly shows that the reaction is zero-order dependence on the aniline concentration. Therefore, the rate is first order on the alcohol and zero order on the aminoarene concentration.

When runs were carried out with different initial catalyst concentrations, a straight line was obtained on plotting the observed rate constants against the different initial catalyst concentrations ($[Ru]_0$ = 1.54 × 10^{-2}, 2.31 × 10^{-2}, and 3.08 × 10^{-2} mol dm^{-3}). Therefore, there is a first-order dependence on the initial concentration of the catalyst. Thus the rate law for the present reaction is expressed by eq 2.

$$\text{rate} = k[Ru]_0^1[\text{aminoarene}]^0[\text{alcohol}]^1 \quad (2)$$

The reaction rates were measured at four temperatures ranging from 120 to 180 °C; k_{obsd} = 1.53 × 10^{-3} min^{-1} at 120 °C, 2.92 × 10^{-3} min^{-1} at 130 °C, 6.78 × 10^{-3} min^{-1} at 150 °C, and 13.18 × 10^{-3} min^{-1} at 160 °C. From the Arrhenius plot of ln k_{obsd} against $1/T$ the activation energy, E_a, of 73.6 kJ mol^{-1} was obtained; $\Delta H^{\ddagger}$ = 70.2 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −123 J mol^{-1} K^{-1}.

Discussion

In order to derive the rate equation (eq 2), the following sequences of elemental reactions (eq 3–6) are considered.

Scheme I

$$ArNH_2 + RuLn \underset{}{\overset{K_1}{\rightleftharpoons}} (ArNH_2)RuLn \quad (3)$$

$$(ArNH_2)RuLn + RCH_2OH \overset{K_2}{\rightleftharpoons} (ArNH_2)(RCHO)RuLnH_2 \quad (4)$$

$$(ArNH_2)(RCHO)RuLnH_2 \xrightarrow[-H_2O]{k_1} (ArN{=}CHR)RuLnH_2 \quad (5)$$

$$(ArN{=}CHR)RuLnH_2 \xrightarrow{k_2} ArNHCH_2R + RuLn \quad (6)$$

We assume that first both the aminoarene and the alcohol coordinate the metal center and then the reaction between them takes place in the coordination sphere. From eq 6 the rate is expressed as follows:

$$\text{rate} = k_2[(ArN{=}CHR)RuLnH_2] \quad (7)$$

Assuming steady-state concentration for the Schiff base intermediate, (ArN=CHR)RuLnH$_2$, and $k_2 \gg k_1$, the rate law for Scheme I would then be

$$\text{rate} = \frac{k_1K_1K_2[ArNH_2][RCH_2OH][Ru]_0}{1 + K_1[ArNH_2] + K_1K_2[ArNH_2][RCH_2OH]} \quad (8)$$

where

$$[Ru]_0 = [RuLn] + [(ArNH_2)RuLn] + [(ArNH_2)(RCHO)RuLnH_2] + [(ArN{=}CHR)RuLnH_2]$$

$[Ru]_0$ is the initial catalyst concentration. If $K_1 \gg 1$ and $K_2 \ll 1$,[17] the rate law becomes

$$\text{rate} = k_1K_2[RCH_2OH][Ru]_0/(1 + K_2[RCH_2OH]) \quad (9)$$

$$= k_1K_2[Ru]_0[RCH_2OH] \quad (10)$$

Thus, by simplifying the equations according to the assumptions, we could obtain the observed rate dependence on the substrates and the initial catalyst concentration.

(17) When $RuCl_2(PPh_3)_3$ was reacted with benzenamine at room temperature in a UV cell ($RuCl_2(PPh_3)_3$, 1.5 × 10^{-2} mol dm^{-3}, and benzenamine, 1.48 mol dm^{-3}, in solvent $CHCl_3$), the absorption at 680 nm of $RuCl_2(PPh_3)_3$ disappeared and the new ones at 510 and 630 nm appeared. These absorptions are assigned to $Ru(PPh_3)(PhNH_2)_3Cl_2$ according to the literature of Poddar and co-workers,[18] showing the coordination of benzenamine is strong. On the other hand, the addition of benzyl alcohol to $RuCl_2(PPh_3)_3$ solution did not change the UV spectrum. Although the reaction conditions are much different from those of the present N-benzylation, the results strongly suggest that $K_1 \gg 1$ and $K_2 \ll 1$ in Scheme I as we assumed.

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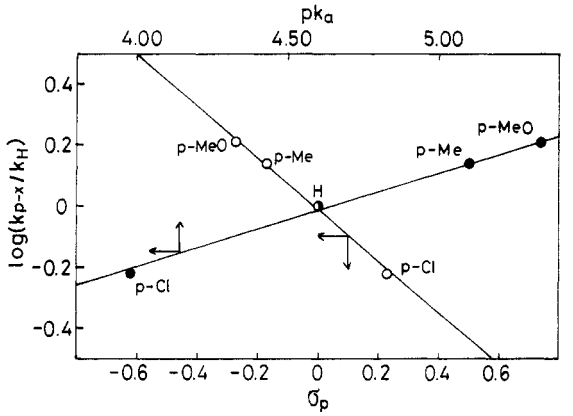
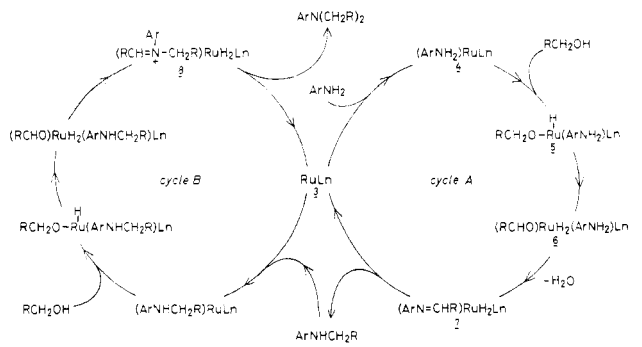


Figure 3. Effect of substituent on the rate constant. $[p\text{-}XC_6H_4NH_2]_0$ = [benzyl alcohol]$_0$ = 1.54 mol dm^{-3}, $[RuCl_2(PPh_3)_3]_0$ = 1.54×10^{-2} mol dm^{-3}, 1,2,3,4-tetrahydronaphthalene (18.1 mL) at 150 °C.

Scheme II



Basicity of Aminoarene. As mentioned above (Table III), the reaction of the aminoarene having high basicity appears to proceed fast. Figure 3 shows the observed rate constants (k_{obsd}) for the N-monobenzylation of various aminoarenes. The plots of the k_{obsd} vs. Hammett's σ_p value and p*Ka* value of the corresponding conjugate acid showed linear relationships. These results clearly indicate that the aminoarene having an electron-releasing group (the aminoarene of high basicity) reacts faster with the alcohol. The results of Figure 3 suggest that the rate-determining step implies a nucleophilic attack of aminoarene (vide infra).

Possible Catalytic Cycle. From these observations, the possible catalytic cycle for the present reaction is described in Scheme II. The active catalyst species, **3**, should contain Cl and PPh_3 as the ligands (Ln in Schemes I and II indicates Cl and PPh_3 ligand), since the complexes without one of these ligands were ineffective (Table II). The aminoarene coordinates to **3** to generate **4** with a large equilibrium constant. The alcohol adds to **4** via alkoxide intermediate **5** into **6**. Such an oxidation pathway has been proposed by several authors.[19-24] The alkoxohydrido complex was recently isolated for the first time by the oxidative addition of an alcohol with alkylgermanium(II) compound.[25] The nucleophilic attack of the coordinated aminoarene to the resulting aldehyde yields the Schiff base complex **7**. This step must be the rate-determining step. The rate of the overall reaction, eq 10, is enhanced with more basic aminoarenes since the rate constant, k_1, of this nucleophilic reaction (eq 5) becomes large. The hydrogenation of the Schiff base intermediate (step from **7** to **3**, generating the product) would be fast, since the Schiff base was not detected as the product in the reaction mixture. Thus, the cycle A produces the N-monoalkylated or benzylated benzenamine and regenerates the active catalyst species, **3**.

After the reaction, *cis*-$RuCl_2(CO)_2(PPh_3)_2$ were isolated from the reaction mixture.[26,27] This carbonyl complex did not show any catalytic activity for the present reaction. This carbonyl complex could be formed by the decarbonylation of the coordinated aldehyde of **6**. The decarbonylations of aldehydes have been intensively studied by several authors and the intermediate including coordinated aldehydes have been postulated.[28-30] As shown in Table I, methanol could not be employed as an effective N-methylation reagent in this procedure. Formaldehyde is well-known to undergo the decarbonylation easily and is often used in preparing carbonyl complexes.[31] In the present reaction methanol easily converted to a carbonyl complex. Indeed, the IR spectrum of the reaction mixture employing methanol as the reactant showed a strong absorption band at 2040 cm^{-1}, indicating the presence of a carbonyl complex.

We did not perform the kinetic measurements for the N,N-dialkylation and N,N-dibenzylation stages. However, we may safely consider the similar catalytic cycle B for these stages. The cycle B could give the product via an iminium intermediate, **8**.

Experimental Section

Materials. The alcohols and the aminoarenes were commercial materials and purified by distillation or recrystallization before use. $RuCl_2(PPh_3)_3$,[32] $RuHCl(CO)(PPh_3)_3$,[33] $RuH_2(PPh_3)_4$,[34] $Ru(CO)_3(PPh_3)_2$,[33] $RhH(PPh_3)_4$,[35] and $RhCl(PPh_3)_3$[36] were prepared by published methods.

Analytical Procedure. The ^1H NMR spectra were obtained at 100 MHz with a JEOL JNM FX-100 or at 220 MHz with a Varian HR-220 spectrometer. The ^{13}C NMR spectra were recorded at 25.05 MHz with a JEOL FX-100 spectrometer, with Me_4Si as an internal standard. IR and UV spectra were measured on a Jasco A-302 and Hitachi EPS-3T spectrophotometer, respectively. Elemental analyses were performed at the Microanalytical Center of Kyoto University. The GLC analysis was performed on a Shimadzu GC-3BT with TCD detector.

General Reaction Procedure. The stainless steel autoclave (50 mL, SUS 304) was used in the reaction. A mixture of aminoarene (40 mmol), alcohol (20 mL), and ruthenium complex (0.4 mmol, 1 mol% based on aminoarene used) was magnetically stirred under argon atmosphere. The autoclave was heated in

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20 min to 180 °C and held at this temperature for 5 h. After cooling, the reaction mixture was submitted to the GLC analysis with 5% Apiezon Grease L supported on Neopak 1A 60–80 mesh (0.3 cm × 3 m). The products were isolated by vacuum fractional distillations. When the products were contaminated with other products, further purification was performed by means of medium-pressure column chromatography (absorbent, Silica Gel 60, 0.040–0.063 mm, 230–400 mesh, Merck No. 9385; eluent, a mixture of hexane and ethyl acetate). The products were identified by means of ^{1}H NMR, ^{13}C NMR, IR, and elemental analysis. The conversion of the substrate and the yield of the product were determined by the internal standard method with biphenyl or bibenzyl according to the caliblation curve obtained for each sample.

Kinetic Measurements. The reactions were performed in a three-necked flask under an argon atmosphere. 1,2,3,4-Tetrahydronaphthalene was used as a solvent and *o*-terphenyl was employed as an internal standard. A small amount of the reaction mixture was sampled at suitable intervals and was subjected to GLC analysis.

***N*-Butyl-4-methylbenzenamine**: colorless oil; bp 74–79 °C (0.5 torr) (1 torr = 133.322 Pa); IR(neat) 1580, 3400 cm^{-1}; ^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.94 (t, 3 H, CH_3), 1.10–1.70 (m, 4 H, 2 CH_2), 2.21 (s, 3 H, CH_3), 3.02 (t, 2 H, CH_2), 3.35 (s, 1 H, NH), 6.40–7.04 (m, 4 H, Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 13.9 (q, CH_3), 20.4 (t, CH_2), 20.4 (q, CH_3), 31.8 (t, CH_2), 44.1 (t, CH_2), 112.9 (d), 126.1 (s), 129.6 (d), 146.3 (s). Anal. Found: C, 81.13; H, 10.77; N, 8.53. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.49; N, 8.58.

***N*,*N*-Dibutyl-4-methylbenzenamine**: pale yellow oil; bp 95–101 °C (0.5 torr); ^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.91 (t, 6 H, 2 CH_3), 1.18–1.80 (m, 8 H, 4 CH_2), 2.21 (s, 3 H, CH_3), 3.18 (t, 4 H, 2 CH_2), 6.45–7.06 (m, 4 H, Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 14.0 (q, 2 CH_3), 20.1 (q, CH_3), 20.4 (t, 2 CH_2), 29.5 (t, 2 CH_2), 51.0 (t, 2 CH_2), 112.3 (d), 124.4 (s), 129.6 (d), 146.1 (s). Anal. Found: C, 82.34; H, 11.73; N, 6.53. Calcd for $C_{15}H_{25}N$: C, 82.12; H, 11.49; N, 6.38.

***N*-Butyl-4-methoxybenzenamine**: ^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.92 (t, 3 H, CH_3), 1.36–1.51 (m, 4 H, 2 CH_2), 2.98 (t, 2 H, CH_2), 3.27 (s, 1 H, NH), 3.66 (s, 3 H, CH_3O), 6.47–6.77 (m, 4 H, Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 14.0 (q, CH_3), 20.4 (t, CH_2), 31.8 (t, CH_2), 4.46 (t, CH_2), 55.7 (q, CH_3O), 113.9 (d), 114.9 (d), 142.9 (s), 151.8 (s).

***N*,*N*-Dibutyl-4-methoxybenzenamine**: pale yellow oil; bp 100–102 °C (0.15 torr); ^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.91 (t, 6 H, 2 CH_3), 1.14–1.74 (m, 8 H, 4 CH_2), 3.15 (t, 4 H, 2 CH_2), 3.68 (s, 3 H, CH_3O), 6.50–6.82 (m, 4 H, Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 14.0 (q, 2 CH_3), 20.5 (t, 2 CH_2), 29.6 (t, 2 CH_2), 51.8 (t, 2 CH_2), 55.7 (q, CH_3O), 114.6 (d), 114.8 (d), 143.3 (s), 151.2 (s). Anal. Found: C, 76.20; H, 10.15; N, 5.74. Calcd for $C_{15}H_{25}NO$: C, 76.54; H, 10.71; N, 5.95.

***N*-Butyl-2-methoxybenzenamine**: ^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.93 (t, 3 H, CH_3), 1.10–1.88 (m, 4 H, 2 CH_2), 3.07 (t, 2 H, CH_2), 3.75 (s, 3 H, CH_3O), 4.10 (s, 1 H, NH), 6.42–6.95 (m, 4 H, Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 13.9 (q, CH_3), 20.4 (t, CH_2), 31.7 (t, CH_2), 43.4 (t, CH_2), 55.2 (q, CH_3O), 109.3 (d), 109.6 (d), 116.0 (d), 121.3 (d), 138.5 (s), 146.7 (s).

***N*,*N*-Dibutyl-2-methoxybenzenamine**: ^{1}H NMR (220 MHz) ($CDCl_3$) δ 0.87 (t, 6 H, 2 CH_3), 1.21–1.33 (m, 4 H, 2 CH_2), 1.38–1.48 (m, 4 H, 2 CH_2), 3.07 (t, 4 H, 2 CH_2), 3.83 (s, 3 H, CH_3O), 6.83–6.95 (m, 4 H, Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 14.1 (q, 2 CH_3), 20.6 (t, 2 CH_2), 29.3 (t, 2 CH_2), 52.7 (t, 2 CH_2), 55.4 (q, CH_3O), 111.8 (d), 120.5 (d), 121.6 (d), 122.4 (d), 140.0 (s), 153.8 (s).

***N*-Butyl-4-chlorobenzenamine**: ^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.95 (t, 3 H, CH_3), 1.45 (m, 4 H, 2 CH_2), 3.00 (t, 2 H, CH_2), 3.51 (s, 1 H, NH), 6.36–7.09 (m, 4 H, Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 13.9 (q, CH_3), 20.3 (t, CH_2), 31.6 (t, CH_2), 43.8 (t, CH_2), 113.6 (d), 121.4 (s), 128.9 (d), 147.1 (s). Anal. Found: C, 66.72; H, 8.23; N, 6.58. Calcd for $C_{10}H_{14}NCl$: C, 65.39; H, 7.68; N, 7.63.

***N*,*N*-Dibutyl-4-chlorobenzenamine**: ^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.94 (t, 6 H, 2 CH_3), 1.40 (m, 8 H, 4 CH_2), 3.18 (t, 4 H, 2 CH_2), 6.44–7.10 (m, 4 H, Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 14.0 (q, 2 CH_3), 20.3 (t, 2 CH_2), 29.3 (t, 2 CH_2), 50.8 (t, 2 CH_2), 112.6 (d), 119.6 (s), 128.6 (d), 146.5 (s). Anal. Found: C, 69.98; H, 9.33; N, 5.72. Calcd for $C_{14}H_{22}NCl$: C, 70.12; H, 9.25; N, 5.84.

***N*-Benzyl-4-methylbenzenamine**: pale yellow oil; Kugelrohr bp 80–88 °C (0.04–0.06 torr); ^{1}H NMR (100 MHz) ($CDCl_3$) δ 2.16 (s, 3 H, CH_3), 3.52 (s, 1 H, NH), 4.11 (s, 2 H, CH_2), 6.46–6.93 (q, 4 H, Ar), 7.02 (m, 5 H, Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 20.3 (q, CH_3), 48.3 (t, CH_2), 112.8 (d), 126.3 (s), 126.8 (d), 127.2 (d), 128.3 (d), 129.5 (d), 139.6 (s), 145.7 (s). Anal. Found: C, 85.76; H, 7.63. Calcd for $C_{14}H_{15}N$: C, 85.23; H, 7.66.

***N*,*N*-Dibenzyl-4-methylbenzenamine**: yellow oil; Kugelrohr bp 92–106 °C (0.1–0.5 torr); ^{1}H NMR (100 MHz) ($CDCl_3$) δ 2.20 (s, 3 H, CH_3), 4.57 (s, 4 H, 2 CH_2), 6.67–6.91 (q, 4 H, Ar), 7.23 (m, 10 H, 2 Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 20.1 (q, CH_3), 54.2 (t, 2 CH_2), 112.6 (d), 125.5 (s), 126.6 (d), 128.4 (d), 128.4 (d), 129.6 (d), 138.6 (s), 146.9 (s). Anal. Found: C, 87.91; H, 7.18. Calcd for $C_{21}H_{21}N$: C, 87.76; H, 7.37.

***N*-Benzyl-4-methoxybenzenamine**: pale yellow oil: bp 138–142 °C (0.1 torr); ^{1}H NMR (100 MHz) ($CDCl_3$) δ 3.54 (s, 1 H, NH), 3.69 (s, 3 H, CH_3O), 4.24 (s, 2 H, CH_2), 6.60–6.71 (q, 4 H, Ar), 7.30 (m, 5 H, Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 49.2 (t, CH_2), 55.7 (q, CH_3O), 114.2 (d), 114.9 (d), 127.1 (d), 127.5 (d), 128.5 (d), 139.8 (s), 142.4 (s), 152.2 (s). Anal. Found: C, 79.12; H, 7.02. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09.

***N*,*N*-Dibenzyl-4-methoxybenzenamine**: yellow oil; bp 174–177 °C (0.2 torr); ^{1}H NMR (100 MHz) ($CDCl_3$) δ 3.61 (s, 3 H, CH_3O), 4.48 (s, 4 H, 2 CH_2), 6.67 (m, 4 H, Ar), 7.20 (m, 10 H, 2 Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 55.0 (t, 2 CH_2), 55.3 (q, CH_3O), 114.5 (d), 114.6 (d), 126.6 (d), 126.7 (d), 128.4 (d), 138.8 (s), 143.5 (s), 151.6 (s). Anal. Found: C, 83.38; H, 6.88. Calcd for $C_{21}H_{21}NO$: C, 83.14; H, 6.98.

***N*-Benzyl-4-chlorobenzenamine**: pale yellow oil; bp 140–144 °C (0.22 torr); ^{1}H NMR (100 MHz) ($CDCl_3$) δ 3.53 (s, 1 H, NH), 4.13 (s, 2 H, CH_2), 6.43–6.96 (q, 4 H, Ar), 7.23 (m, 5 H, Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 48.1 (t, CH_2), 113.8 (d), 121.8 (s), 127.2 (d), 128.5 (d), 128.9 (d), 138.8 (s), 146.5 (s). Anal. Found: C, 73.66; H, 5.63. Calcd for $C_{13}H_{12}NHCl$: C, 71.72; H, 5.56.

***N*,*N*-Dibenzyl-4-chlorobenzenamine**: yellow crystals; Kugelrohr bp 93–97 °C (0.15 torr); ^{1}H NMR (100 MHz) ($CDCl_3$) δ 4.60 (s, 4 H, 2 CH_2), 6.65–7.02 (q, 4 H, Ar), 7.26 (m, 10 H, 2 Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 54.4 (t, 2 CH_2), 113.5 (d), 126.3 (d), 126.9 (d), 128.5 (d), 128.8 (d), 137.9 (s), 138.0 (s), 147.4 (s). Anal. Found: C, 78.56; H, 5.95. Calcd for $C_{20}H_{18}NCl$: C, 78.05; H, 5.89.

***N*-Ethyl-*N*-octylbenzenamine**: pale yellow oil; bp 95–100 °C (0.07 torr); ^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.88–1.57 (m, 18 H), 3.13–3.42 (m, 4 H, 2 NCH_2), 6.60–7.25 (m, 5 H, Ar); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 12.3 (q), 14.1 (q), 22.7 (t), 27.2 (t), 27.5 (t), 29.3 (t), 29.5 (t), 31.9 (t), 45.0 (t), 50.6 (t), 111.9 (d), 115.4 (d), 129.1 (d), 147.8 (s). Anal. Found: C, 82.14; H, 11.92. Calcd for $C_{16}H_{27}N$: C, 82.34; H, 11.66.

Registry No. 1 (x = 4-Me, R = Bu), 31144-33-9; 1 (x = 4-MeO, R = Bu), 82749-62-0; 1 (x = 2-MeO, R = Bu), 82749-65-3; 1 (x = 4-Cl, R = Bu), 67655-26-9; 1 (x = 4-Me, R = $PhCH_2$), 5459-79-0; 1 (x = 4-MeO, R = $PhCH_2$), 18613-55-3; 1 (x = 4-Cl, R = $PhCH_2$), 15429-21-7; 1 (x = H, R = Et), 91-66-7; 1 (x = H, R = Pr), 2217-07-4; 1 (x = H, R = Bu), 613-29-6; 1 (x = H, R = $PhCH_2$), 91-73-6; 1 (x = H, R = Me), 121-69-7; 2 (x = 4-Me, R = Bu), 10387-24-3; 2 (x = 4-MeO, R = Bu), 61829-43-4; 2 (x = 2-MeO, R = Bu), 65570-20-9; 2 (x = 4-Cl, R = Bu), 5441-81-6; 2 (x = 4-Me, R = $PhCH_2$), 5405-15-2; 2 (x = 4-MeO, R = $PhCH_2$), 17377-95-6; 2 (x = 4-Cl, R = $PhCH_2$), 2948-37-0; 2 (x = H, R = Pr), 622-80-0; 2 (x = H, R = Bu), 1126-78-9; 2 (x = H, R = $PhCH_2$), 103-32-2; 2 (x = H, R = Me), 100-61-8; 2 (x = H, R = *i*-Pr), 768-52-5; 2 (x = H, R = *sec*-Bu), 6068-69-5; 2 (x = 4-MeO, R = H), 104-94-9; 2 (x = 4-Cl, R = H), 106-47-8; 2 (x = 2-MeO, R = H), 90-04-0; 2 (x = H, R = Et), 103-69-5; 2 (x = 4-Me, R = H), 106-49-0; $RuCl_2(PPh_3)_3$, 15529-49-4; $RuHCl(CO)(PPh_3)_3$, 16971-33-8; $RuH_2(PPh_3)_4$, 19529-00-1; $Ru(CO)_3(PPh_3)_2$, 14741-36-7; $RuCl_3 \cdot nH_2O$, 10049-08-8; $RhH(PPh_3)_4$, 18284-36-1; $RhCl(PPh_3)_3$, 14694-95-2; $Ru(PPh_3)(PhNH_2)_3Cl_2$, 51405-71-1; *N*-ethyl-*N*-octylbenzenamine, 91191-65-0; ethanol, 64-17-5; 1-propanol, 71-23-8; 1-butanol, 71-36-3; benzyl alcohol, 100-51-6; methanol, 67-56-1; 2-propanol, 67-63-0; 2-butanol, 78-92-2; aniline, 62-53-3.