Ruthenium Catalyzed Reduction of Nitroarenes and Azaaromatic Compounds Using Formic Acid

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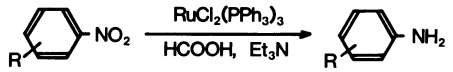
Various nitroarenes having chloro, methyl, or methoxy substituents were reduced to the corresponding aminoarenes in high yields using formic acid in the presence of a catalytic amount of $RuCl_2(PPh_3)_3$. For example, 4-chloronitrobenzene was converted in 99% conversion with 98% selectivity at 125 °C for 5 h. 4-Nitroacetophenone was reduced chemoselectively to 1-(4-nitrophenyl)ethanol in 74% isolated yield under the same reaction conditions. Formic acid could also be employed as reductant for hydrogenation of heterocyclic compounds such as quinoline, indole, and quinoxaline in the presence of the ruthenium catalyst. 2-Methylquinoline was hydrogenated to 1,2,3,4-tetrahydro-2-methylquinoline in 93% conversion with 100% selectivity.

Reduction of nitroarenes is one of the most convenient methods of producing the aminoarenes which are the primary source for various aromatic nitrogen compounds. Molecular hydrogen or hydrogen chloride is generally employed as the hydrogen source in the reaction. However, applications of other hydrogen sources have been developed. As for the reduction of nitroarenes, water was combined with carbon monoxide as the hydrogen source in the water gas shift reaction (WGSR),[1] and amines,[2] alcohols,[3] and cyclohexene[4] were employed as hydrogen donors in transfer hydrogenation.

We have been using formic acid, which is easily derived from synthesis gas, in organic synthesis and have already reported its effectiveness for hydrogenation of carbonyl compounds.[5] In this paper, we describe the reduction of nitroarenes and azaaromatic compounds with formic acid in the presence of a homogeneous ruthenium catalyst.

Results and Discussion

Reduction of Nitroarenes. Nitroarenes were reduced to aminoarenes in high yields using formic acid in the presence of a catalytic amount of $RuCl_2(PPh_3)_3$ (Eq. 1, Table 1). Nitrobenzene was converted to aniline



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in 97% conversion with 97% selectivity. Methyl, methoxy, and chloro substituents at 2- or 4-position did not suppress the reaction. These observations were almost identical with the results reported by Knifton[6] who used molecular hydrogen as reductant in the presence of $RuCl_2(PPh_3)_3$. In the reduction of 4-nitroacetophenone by our system, 1-(4-nitrophenyl)ethanol was the major product, indicating that the reaction is chemoselective (Eq. 2). Knifton reported that 4-aminoacetophenone was mainly formed by molecular hydrogen in the presence of $RuCl_2(PPh_3)_3$ (A in Eq. 3)[7] and Heck also reported that 4-nitroacetophenone was reduced to 4-aminoacetophenone by use of triethylammonium formate in the presence of Pd/C (B in Eq. 3).[8] Furthermore, there have been few reports on the transition metal-catalyzed selective reduction of a carbonyl group in the presence of a nitro group. Tsuji *et al.*[9] have reported that $RuCl_2(PPh_3)_3$ catalyzed the selective reduction of benzaldehyde to benzyl alcohol in the presence of nitrobenzene by molecular hydrogen.

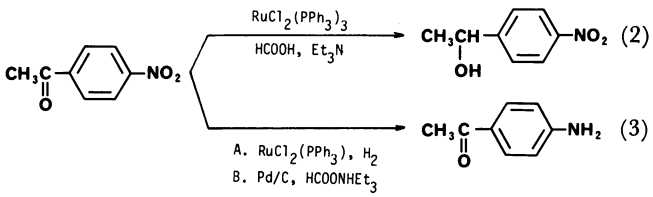


Table 1. Ruthenium-catalyzed reduction of several nitroarenes using formic acid[a]

Run	Nitroarene R = [b]	Product	Conv. of [c] nitroarene/%	Selectivity [d] to product/%
1	H	Aniline	97	97
2	2-Methyl	2-Methylaniline	99	96
3	2-Methoxy	2-Methoxyaniline	94	91
4	2-Chloro	2-Chloroaniline	100	94
5	4-Methyl	4-Methylaniline	86	96
6	4-Methoxy	4-Methoxyaniline	100	97
7	4-Chloro	4-Chloroaniline	99	98
8[e]	4-Acetyl	1-(4-Nitrophenyl)-ethanol		74[f]

a) The mixture of nitroarene (10 mmol), formic acid (33 mmol), Et_3N (35 mmol), ethanol (5 ml), and $RuCl_2(PPh_3)_3$ (0.05 mmol) was stirred at 125 °C for 5 h. b) See Eq. 1. c) Determined by GLC based on the amount of nitroarene used. d) Determined by GLC based on the conversion of nitroarene. e) Formic acid (20 mmol) was used, for 2.5 h. f) The figure in parenthesis is the isolated yield.

Figure 1 shows the pressure change during the reduction of nitrobenzene using formic acid in the presence of $RuCl_2(PPh_3)_3$. This result shows that only a little evolution of molecular hydrogen occurred in the early stage of the reaction.

This reaction proceeded without solvent with high selectivity but the use of solvent hastened the reaction. In Fig. 2, the reaction temperature *vs.* conversion of nitrobenzene is shown. The conversions were affected by the solvent employed. Over 90% conversion was attained at 125 °C in ethanol and at 180 °C in dioxane. Methanol, 2-propanol, and ethanol–benzene were also good solvents for this reaction (Table 2). Thus, alco-

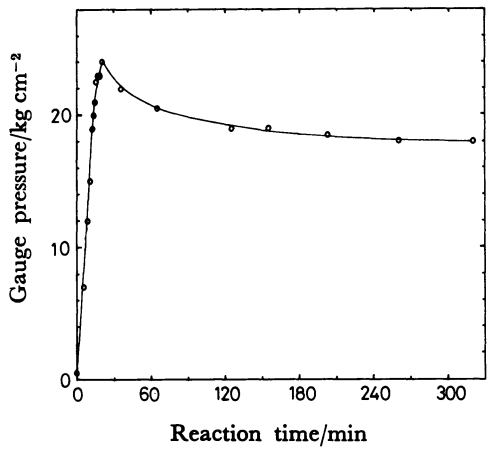


Fig. 1. Ruthenium-catalyzed Reduction of Nitrobenzene using Formic Acid. The pressure change during the reaction.
The mixture of nitrobenzene(10 mmol), formic acid (33 mmol), Et_3N (11.7 mmol), ethanol (5 ml), and $RuCl_2(PPh_3)_3$ (0.05 mmol) was heated at 125 °C in a 50 ml stainless steel autoclave.

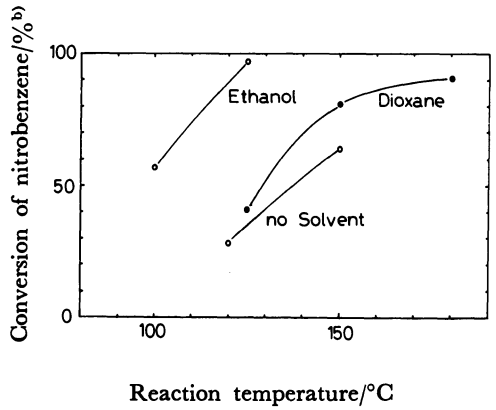


Fig. 2. Ruthenium-catalyzed Reduction of Nitrobenzene using Formic Acid.[a] Effect of Solvent.
a) The mixture of nitrobenzene(10 mmol), formic acid (33 mmol), Et_3N (35 mmol), $RuCl_2(PPh_3)_3$ (0.05 mmol) and solvent (5 ml) was heated for 5 h. b) Determined by GLC based on the amount of nitrobenzene used.

holic solvents gave good results. It is well known that alcohols are good hydrogen donor in the transfer hydrogenation. However, in the present reaction, removal of formic acid from ethanol solution gave aniline in only 2% yield. Therefore, the contribution of the transfer hydrogenation from ethanol was considered negligible in the reaction.

In the present reaction, a base was necessary for high conversion and good selectivity. Runs 14—17 indicate that the presence of triethylamine improved the conversion of nitrobenzene and the selectivity to aniline. *N*-Ethylaniline was obtained as a by-product.[10] The best result was realized in Run 17. Potassium hydroxide showed the same effect as triethylamine. However, good reproducibility was not obtained, since the reaction was heterogeneous.

Catalytic activities of several ruthenium compounds were examined, the results are listed in Table 4. $RuCl_2(PPh_3)_3$ was the most effective catalyst precursor and gave the best result. The highest turnover frequency was 350 (times/5 h) (Run 24). $RuH_2(PPh_3)_4$ and $RuHCl(PPh_3)_3$ also showed catalytic activities with triethylamine, but the conversions of nitrobenzene were

Table 2. Ruthenium-catalyzed reduction of nitrobenzene in various solvents[a]

Run	Solvent	Conversion of[b] nitrobenzene/%	Selectivity[c] to aniline/%
1	Ethanol	97	97
9	Dioxane	41	100
10	Methanol	87	91
11	2-Propanol	80	96
12[d]	Ethanol-benzene	92	100
13[e]	no solvent	28	93

a) The mixture of nitrobenzene (10 mmol), formic acid (33 mmol), Et_3N (35 mmol), $RuCl_2(PPh_3)_3$ (0.05 mmol), and solvent (5 ml) was stirred at 125 °C for 5 h. b) Determined by GLC based on the amount of nitrobenzene used. c) Determined by GLC based on the conversion of nitrobenzene. d) Ethanol (2.5 ml) and benzene (2.5 mmol) were used as solvents. e) Reaction temperature: 120 °C.

Table 3. Ruthenium-catalyzed reduction of nitrobenzene. Effect of the base[a]

Run	Base (mmol)	Reaction time/h	Conversion of[b] nitrobenzene/%	Selectivities[c]	
				Aniline	*N*-Ethylaniline
14		5	66	39	21
15	Et_3N (1.10)	5	76	57	16
16	Et_3N (10.0)	2.5	96	88	10
17	Et_3N (35.0)	2.5	96	95	4
18	Pyridine (10.0)	2.5	61	69	0
19	Et_2NH (10.0)	2.5	71	100	0
20	*n*-$BuNH_2$ (10.0)	2.5	41	98	0
21	TMED[d] (10.0)	2.5	48	85	0
22	KOH (10.0)	2.5	94	90	10

a) The mixture of nitrobenzene (10 mmol), formic acid (33 mmol), ethanol (5 ml), $RuCl_2(PPh_3)_3$ (0.05 mmol), and the base was stirred at 125 °C. b) Determined by GLC based on the amount of nitrobenzene used. c) Determined by GLC based on the conversion of nitrobenzene. d) TMED: *N,N,N',N'*-Tetramethylethylenediamine.

low without the base (Runs 27 and 29). In order to investigate the role of chloro ligand on the catalyst precursor, $Et_3N \cdot HCl$ (0.1 mmol) was combined with $RuH_2(PPh_3)_4$ in the reduction of nitrobenzene (Run 30). However this resulted in only a slight improvement of the conversion and the selectivity.

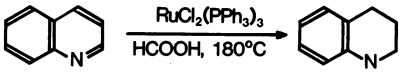
There have been several ruthenium-catalyzed reduction of nitroarene. $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$ showed good catalytic activities with molecular hydrogen.[6] $Ru_3(CO)_{12}$,[1a,c] $Ru(acac)_3$,[1a] $[Ru(COD)py_4](BPh_4)_2$,[1b] and $H_4Ru_4(CO)_{12}$[1c] were employed as catalysts under water gas shift reaction conditions (with water and carbon monoxide pressure). $RuCl_3 \cdot 3H_2O$ catalyzed the transfer hydrogenation with indoline[2] and $Ru_3(CO)_{12}$ were used in the phase transfer reaction.[11] The present reduction system using formic acid shows the same results as (or better results than) the above catalytic systems under similar reaction conditions. Furthermore, in the procedure, an excess reductant is not necessary and 1.1 equiv formic acid is sufficient for obtaining high yields of the products. Formic acid is easy to handle as compared with molecular hydrogen and after the reaction formic acid was completely decomposed into carbon dioxide and hydrogen.

TABLE 4. RUTHENIUM-CATALYZED REDUCTION OF NITROBENZENE. CATALYTIC ACTIVITIES OF SEVERAL RUTHENIUM COMPOUNDS[a]

Run	Catalyst	Conversion of[b] nitrobenzene/%	Selectivity[c] to aniline/%
23		16	31
1	$RuCl_2(PPh_3)_3$	97	97
24[d]	$RuCl_2(PPh_3)_3$	49	70
25	$RuCl_3 \cdot nH_2O$	100	77
26	$RuHCl(PPh_3)_3$	71	94
27[e]	$RuHCl(PPh_3)_3$	27	82
28	$RuH_2(PPh_3)_4$	69	93
29[e]	$RuH_2(PPh_3)_4$	39	63
30[f]	$RuH_2(PPh_3)_4$	73	99

a) The mixture of nitrobenzene (10 mmol), formic acid (33 mmol), Et_3N (35 mmol), ethanol (5 ml), and a catalyst (0.05 mmol) was stirred at 125 °C for 5 h. b) Determined by GLC based on the amount of nitrobenzene used. c) Determined by GLC based on the conversion of nitrobenzene. d) Catalyst, 0.01 mmol. e) Without Et_3N. f) $Et_3N \cdot HCl$ (0.1 mmol) was added.

Reduction of Azaaromatic Compounds. Reductions of azaaromatic compounds by molecular hydrogen in the presence of the transition metal catalyst have been reported.[12] As for the ruthenium-catalyzed reaction, $RuCl_2(CO)_2(PPh_3)_2$ and $H_4Ru_4(CO)_{12}$[12d] catalyzed the reduction of quinoline derivatives. Ruthenium on carbon was used to the reduction of 2,3-benzopyrrole[12e] and the same catalyst was employed with hydrazine as the hydrogen source.[12c] Azaaromatic compounds were also reduced under WGSR conditions.[12d] The transfer hydrogenation is not applicable to azaaromatic compounds, since 1,2,3,4-tetrahydroquinoline, indoline, and their derivatives were very good hydrogen donors in the presence of transition metal catalysts.[13]



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The formic acid-ruthenium catalyst was applied to the reduction of several azaaromatic compounds. The results are listed in Table 5. Formic acid was employed in stoichiometric amounts. In these reactions, different from the case of the nitroarenes, the addition of the base was not necessary for a high yield of the product. However, a higher reaction temperature was required for the high conversion (Runs 31 and 32). Thus, 1,2,3,4-tetrahydroquinoline was obtained in a reasonable yield by the reaction at 180 °C (Run 32). Prolonging the reaction time (18 h) increased the conversion. The hydrogenation occurred only at the azaaromatic ring. Other *N*-heterocyclic compounds were also hydrogenated at the *N*-heterocyclic rings (Runs 34—38). For indole derivatives, the conversions were rather low under the reaction conditions employed (Runs 36 and 37).

The highest catalytic activity was shown by

TABLE 5. RUTHENIUM-CATALYZED REDUCTION OF AZAAROMATIC COMPOUNDS USING FORMIC ACID[a]

Run	Substrate	Product	Conversion of[b] substrate/%	Selectivity[c] to product/%
31[d]	Quinoline	1,2,3,4-Tetrahydroquinoline	52	83
32	Quinoline	1,2,3,4-Tetrahydroquinoline	84	83
33[e]	Quinoline	1,2,3,4-Tetrahydroquinoline	95	80
34	2-Methylquinoline	1,2,3,4-Tetrahydro-2-methylquinoline	93	100
35	4-Methylquinoline	1,2,3,4-Tetrahydro-4-methylquinoline	85	99
36[f]	Indole	Indoline	53	83
37[f]	2-Methylindole	2-Methylindoline	50	80
38[f]	Quinoxaline	1,2,3,4-Tetrahydroquinoxaline	91	83
39	Isoquinoline		0	
40	Pyridine		0	

a) The mixture of a substrate (40 mmol), formic acid (80 mmol), and $RuCl_2(PPh_3)_3$ (0.1 mmol) was stirred at 180 °C for 6 h. b) Determined by GLC based on the amount of the substrate used. c) Determined by GLC based on the conversion of the substrate. d) Reaction temperature: 150 °C. e) Reaction time: 18 h. f) Benzene (20 ml) was used as solvent.

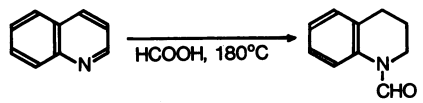
Table 6. Ruthenium-catalyzed reduction of quinoline. Catalytic activities of several ruthenium compounds[a]

Run	Catalyst	Conversion of[b] quinoline/%	Selectivity to[c] 1,2,3,4-THQ/%
31	$RuCl_2(PPh_3)_3$	84	83
41	$RuCl_3 \cdot nH_2O + 3PPh_3$	83	82
42	$RuCl_3 \cdot nH_2O$	71	45
43	$Ru_3(CO)_{12}$	82	63
44	$RuH_2(PPh_3)_4$	12	50
45	$Ru(CO)_3(PPh_3)_2$	35	11

a) The mixture of quinoline (40 mmol), formic acid (80 mmol), and a catalyst (0.1 mmol) was stirred at 180 °C for 6 h. b) Determined by GLC based on the amount of quinoline used. c) Determined by GLC based on the conversion of quinoline. 1,2,3,4-THQ: 1,2,3,4-Tetrahydroquinoline.

$RuCl_2(PPh_3)_3$. An almost same equal activity was realized with $RuCl_3 \cdot nH_2O + 3PPh_3$ (Run 41). $Ru_3(CO)_{12}$ and $RuCl_3 \cdot nH_2O$ had some catalytic activities. However, $RuH_2(PPh_3)_4$ and $Ru(CO)_3(PPh_3)_2$ did not catalyze the reaction very much.

When the reaction was carried out with formic acid in the absence of the ruthenium catalyst, 1,2,3,4-tetrahydro-1-quinolinecarbaldehyde was isolated in only low yield (20%) (Eq. 5). This result suggests that the decomposition of formic acid is sluggish without the ruthenium catalyst.



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Other aromatic compounds were employed as substrates. However, pyrene, anthracene, phenanthrene, naphthalene, 2-methylnaphthalene, anisole, and benzene were almost inactive in the present hydrogenation by $RuCl_2(PPh_3)_3$-HCOOH system at 180 °C.

Experimental

All substrates, solvents and amines were obtained from commercial products and were freshly distilled *in vacuo* or recrystallized before use. Formic acid (99%), KOH, K_2CO_3, and $NH_4 \cdot HCl$ were used without further purification. The catalysts; $RuCl_2(PPh_3)_3$,[14] $RuHCl(PPh_3)_3$,[15] $RuH_2(PPh_3)_4$,[16] $Ru_3(CO)_{12}$,[16] and $Ru(CO)_3(PPh_3)_2$[18] were prepared by methods reported in the literature.

GLC analysis was performed on a Shimadzu GC-3BT apparatus. ^1H NMR spectra were obtained at 100 MHz with a JEOL JNM FX-100 pulsed Fourier Transform spectrometer or at 300 MHz with a Nicoled NTC-300 spectrometer equipped with a 1180E computer system. The JEOL JNM FX-100 pulsed Fourier Transform spectrometer was also used to measure the 25.05 MHz ^{13}C NMR spectra. The IR spectra were measured on a Hitachi model 215 grating spectrophotometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. The mass spectra were recorded on a JMS OlSG mass spectrometer.

Reduction of Nitroarenes. A nitroarene (10 mmol), formic acid (33 mmol), a ruthenium complex (0.05 mmol), Et_3N (35 mmol), and ethanol (5 ml) as an solvent were placed in a 50 ml stainless steel autoclave with a magnetic stirring bar. The air was replaced with argon. Then the autoclave was heated to 125 °C in 20 min and held at this temperature for 5 h. The reaction was terminated by rapid cooling. The reaction products were isolated by distillation or extraction with HCl aq (10%). The identification of the products were performed by comparing the spectral data(^{13}C, ^1H NMR and IR spectra) with those of authentic samples. The conversions of the substrate and the selectivities to the products were determined by GLC (3 mmϕ×3 m column packed with 10% Versamid 900 on Neopak 1A 60—80 mesh or 5% Apiezon Grease L on Neopak 1 A 60—80 mesh) by the internal standard methods.

1-(4-Nitrophenyl)ethanol: Isolated by medium-pressure column chromatography (silica gel, Merck No.9385, hexane–ethyl acetate as the eluent). IR (neat) 3360 (ν_{OH}), 1615 and 1350 (ν_{NO_2}), 1095 (ν_{COH}), and 870 cm^{-1} (ν_{CN}). ^1H NMR ($CDCl_3$) (100 MHz) δ=1.49 (d, 3H, C<u>H</u>$_3$), 3.75 (s, 1H, O<u>H</u>), 4.96 (q, 1H, C<u>H</u>), and 6.38—8.11 (m, 4H, phenyl ring). ^{13}C NMR ($CDCl_3$) δ=25.36 (q), 69.34 (d), 123.58 (d, 2C), 126.17 (d, 2C), 146.89 (s), and 153.47 (s).

Reduction of Azaaromatic Compounds. A 100 ml stainless steel autoclave with a magnetic stirrer bar was used in the reaction. A typical reaction with quinoline and formic acid will be described here to exemplify the general procedure adopted. A mixture of quinoline (40 mmol), formic acid (80 mmol), and $RuCl_2(PPh_3)_3$ (0.1 mmol) was stirred magnetically at 180 °C under an argon atmosphere for 6 h. In the reaction with indole, 2-methylindole, and quinoxaline, benzene (20 ml) was used as solvent.

Reaction products were isolated by distillation or column chromatography (silica gel). 1,2,3,4-Tetrahydroquinoline and indoline were identified by comparing the ^1H and ^{13}C NMR spectra with those of authentic samples. 1,2,3,4-Tetrahydro-2-methylquinoline,[19] 2,3-dihydro-2-methylindole,[20] and 1,2,3,4-tetrahydroquinoxaline[21] were identified by comparison of ^1H NMR and/or IR spectra with those of the literature. These products were further confirmed by their ^{13}C NMR spectra. 1,2,3,4-Tetrahydro-4-methylquinoline was determined by ^1H and ^{13}C NMR, IR, mass spectra, and elemental analysis. The analytical data are shown below.

1,2,3,4-Tetrahydro-2-methylquinoline: ^1H NMR (300 MHz) ($CDCl_3$) δ=1.15 (d, 3H, C<u>H</u>$_3$, J=6.3 Hz), 1.55 (d of d of d of d, 1H, axial proton on 3C, J_{gem}=12.7 Hz, J=11.3, 9.9, and 5.4 Hz), 1.87 (d of d of d of d, 1H, equatorial proton on 3C, J_{gem}=12.7 Hz, J=5.6, 3.6, and 3.3 Hz), 2.68 (d of d of d, 1H, equatorial proton on 4C, J_{gem}=16.4 Hz, J=5.4 and 3.6 Hz), 2.79 (d of d of d, 1H, axial proton on 4C, J_{gem}=16.4 Hz, J=11.3 and 5.6 Hz), 3.33 (q of d of d, 1H, proton on 2C (axial), J=9.9, 6.3, and 3.3 Hz), 3.55 (s, 1H, N<u>H</u>), 6.42 (d of d, 1H, J=7.2 and 0.9 Hz), 6.57 (t of d, 1H, J=7.2 and 0.9 Hz), 6.92 (d, 1H, J=7.2 Hz), and 6.93 (t, 1H, J=7.2 Hz). ^{13}C NMR ($CDCl_3$): δ=22.5 (q), 26.5 (t), 30.0 (t), 47.0 (d), 113.7 (d), 116.6 (d), 120.7 (s), 126.3 (d), 128.9 (d), and 144.3 (s).

2-Methylindoline: ^{13}C NMR ($CDCl_3$) δ=22.1 (q), 37.6 (t), 55.0 (d), 108.8 (d), 118.1 (d), 124.3 (d), 126.8 (d), 128.5 (s), and 150.6 (s).

1,2,3,4-Tetrahydroquinoxaline: ^{13}C NMR ($CDCl_3$) δ=41.2 (t), 114.5 (d), 118.4 (d), and 133.6 (s).

1,2,3,4-Tetrahydro-4-methylquinoline: ^1H NMR (300 MHz) ($CDCl_3$) δ=1.22 (d, 3H, C<u>H</u>$_3$, J=7.2 Hz), 1.58 (d of d of d of d, 1H, equatorial proton on 3C, J_{gem}=12.0 Hz, J=7.0, 7.0, and 3.6 Hz), 1.88 (d of d of d of d, 1H, axial proton on 3C, J_{gem}=12.0 Hz, J=8.4, 7.0, and 4.2 Hz), 2.83 (q of d, 1H, proton on 4C, J=7.2 and 7.2 Hz), 3.11 (d of d of d, 1H, equatorial proton on 2C, J_{gem}=11.5 Hz, J=7.0 and 4.2 Hz), 3.17 (d of d of d, 1H, axial proton on 2C, J_{gem}=11.5 Hz, J=8.4 and 3.6 Hz), 3.64 (s, N<u>H</u>), 6.34 (d, 1H, J=7.5 Hz), 6.58 (t, 1H, J=7.5 Hz), 6.91 (t, 1H, J=7.5 Hz), and 6.99 (d, 1H, J=7.5 Hz). ^{13}C NMR

($CDCl_3$) δ=22.6 (q), 29.8 (d), 30.2 (d), 38.9 (t), 114.0 (d), 116.7 (d), 126.3 (s), 126.6 (d), 128.2 (d), and 144.1 (s). IR (neat) 3390 cm^{-1} (ν_{NH}). MS (m/z) 147 (M^+) and 132 (M^+-CH_3). Calcd for $C_{10}H_{13}N$: C, 81.58; H, 8.90; N, 9.51%. Found: C, 82.07; H, 8.94; N, 9.72%.

Reaction of Quinoline with Formic Acid without Catalyst. Quinoline (40 mmol) and formic acid (80 mmol) were stirred magnetically in a 100 ml stainless steel autoclave at 180 °C for 6 h under an argon atmosphere. The reaction product was distilled and a colorless oil was obtained.

1,2,3,4-Tetrahydro-1-quinolinecarbaldehyde: Colorless oil, bp 94—98 °C/0.07 mmHg (1 mmHg≈133.322 Pa). ^1H NMR (100 MHz) ($CDCl_3$) δ=4.82 (quint, 2H), 2.71 (t, 2H), 3.71 (t, 2H), 7.07 (s, 4H), and 8.68 (s, 1H). ^{13}C NMR ($CDCl_3$) δ=22.1 (t), 27.1 (t), 40.1 (t), 116.8 (d), 124.2 (d), 126.9 (d), 128.5 (s), 129.5 (d), 137.1 (s), and 160.7 (d). IR (neat) 1670 cm^{-1} (ν_{CO}). MS (m/z) 161 (M^+), 132 (M^+–CHO). Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69%. Found: C, 74.81; H, 6.91; N, 8.70%.

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