B. At 100 °C. A solution of 1 g (0.9 mmol) of **3a** in 40 ml of acetic acid was treated with 2 g of zinc powder at 100 °C for 60 min and worked up as described above, 0.40 g of the crude of **5d.** The purification of the crude product was carried out by column chromatography on silica gel using chloroform, affording 0.34 g (63%) of **5d:** mp 181–183 °C (lit.[7] mp 181–183 °C); colorless plates (petroleum ether); IR (KBr). 3550, 3440 cm^{-1} (OH); NMR ($CDCl_3$) δ 1.45 [18 H, s, $(CH_3)_3$], 4.78 (2 H, s, OH), 6.67 (2 H, d, J_{ac} = 7.61 Hz), 7.15 (2 H, d, J_{ab} = 2.21 Hz), 7.36 (2 H, dd, J_{ab} = 2.25 Hz, J_{ac} = 7.65 Hz, aromatic protons).

Reduction of 5a. To a solution of 0.55 g (1.0 mmol) of **5a** was added 1 g of zinc powder. The reaction mixture was heated at 100 °C for 60 min, and worked up as described above. The compound **5d** was obtained in 70% yield, mp 181–183 °C.

Reduction of 3b. A solution of 2.4 g (1.6 mmol) of **3b** in 50 ml of acetic acid was treated with 4.5 g of zinc powder at 20 °C for 30 min and worked up as described above to give 1.89 g (85.9%) of **5b:** mp 55–59 °C; colorless, crystalline powder (AcOH–H_2O); IR (KBr) 3530 cm^{-1} (OH); NMR ($CDCl_3$) δ 1.42 [18 H, s, $(CH_3)_3$], 5.80 (2 H, s, OH), 7.31 (2 H, d, J = 2.25 Hz), 7.74 (2 H, d, J = 2.25 Hz, aromatic protons).

Anal. Calcd for $C_{20}H_{24}O_2Br_2$: c, 52.65; H, 5.30. Found: C, 52.87; H, 5.44.

Reduction of 3c. A solution of 1.95 g (1.3 mmol) of **3c** in 40 ml of acetic acid was treated with 4 g of zinc powder and worked up as described above. Similarly 1.02 g (87.6%) of **5b** was obtained.

Reduction of 3d. Similarly 85 mg (86%) of **5c** was obtained from 100 mg (0.1 mmol) of **3d** with 200 mg of zinc powder in 5 ml of acetic acid. **5c:** mp 54–58 °C; colorless, crystalline powder; IR (KBr) 3540 cm^{-1} (OH); NMR ($CDCl_3$) δ 1.45 [18 H, s, $(CH_3)_3$], 5.86 (2 H, s, OH), 7.20–7.45 (4 H, m, aromatic protons).

Anal. Calcd for $C_{20}H_{24}O_2Cl_2$: C, 65.40; H, 6.59. Found: C, 65.03; H, 6.52.

Formation of 3,5,3′,5′-Tetra-*tert*-butylphenoquinone (4) from 2,6-Di-*tert*-butyl-4-bromophenol (1i). A solution of 5 g (17.5 mmol) of **1i** in 30 ml of the Claisen alkali reagent was heated at 80 °C for 60 min and worked up as described above to give 3.4 g (95%) of **4** as orange needles, mp 241–243 °C (lit. mp 240–241 °C).

Preparation of 2-*tert*-Butyl-4,6-diiodophenol (1e). To a solution of 11 g (73.2 mmol) of 2-*tert*-butylphenol in 30 ml of acetic acid was added at 40 °C a solution of 25 g (154 mmol) of ICl in 20 ml of acetic acid. After the reaction mixture was heated at 70 °C for 5 min, it was poured into a large amount of water and extracted three times with 100 ml of benzene. The extract was dried over sodium sulfate and evaporated in vacuo to leave the dark brown residue which was chromatographed on silica gel using benzene as an eluent affording 20 g (68%) of **1e** as colorless needles (EtOH): mp 55.5–57.5 °C; IR (KBr) 3500 cm^{-1} (OH); NMR ($CDCl_3$) δ 1.35 [9 H, s, $(CH_3)_3$], 5.50 (1 H, s, OH), 7.46 (1 H, d, J = 2.25 Hz), 7.80 (1 H, d, J = 2.25 Hz, aromatic protons).

Anal. Calcd for $C_{10}H_{12}OI_2$: C, 29.87; H, 3.01. Found: C, 29.42; H, 2.29.

Registry No.—**1a,** 118-79-6; **1b,** 609-22-3; **1c,** 13395-86-3; **1d,** 60803-25-0; **1e,** 60803-26-1; **1f,** 60803-27-2; **1g,** 15460-12-5; **1h,** 60803-28-3; **1i,** 1139-52-2; **3a,** 60828-71-9; **3b,** 60803-32-9; **3c,** 60803-34-1; **3d**$_1$, 60803-37-4; **3d**$_2$, 60803-39-6; **5a,** 60828-70-8; **5b,** 60803-31-8; **5c,** 60803-38-5; **5d,** 60803-40-9; 2-*tert*-butylphenol, 88-18-6.

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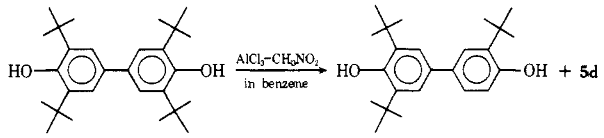

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Transfer Hydrogenation and Transfer Hydrogenolysis. 13. Hydrogen Transfer from Cyclic Amines to Aromatic Nitro Compounds Catalyzed by Noble Metal Salts

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Noble metal salts were found to catalyze the homogeneous transfer hydrogenation of nitrobenzenes to anilines in good yields using indoline as a hydrogen donor. Tetrahydroquinoline, piperidine, and pyrrolidine also showed relatively high hydrogen donating ability. $RuCl_3 \cdot H_2O$ and $RhCl_3 \cdot 3H_2O$ had high and $PdBr_2$ and $PdCl_2$ moderate catalytic activity. A mechanistic pathway is proposed in which the initial formation of Rh(I) species, the coordination of nitrobenzene to Rh(I) species, and the hydrogen transfer from indoline to nitrobenzene on the metal are involved. Nitrosobenzene was detected as an intermediate.

It has been reported that the reduction of a nitro group by molecular hydrogen is catalyzed by several heterogeneous[1] and homogeneous catalysts.[2] However, the catalytic reduction of a nitro group by the hydrogen transfer from organic compounds (transfer hydrogenation) has been scarcely reported. So far as we know, the only example seems to be that cyclohexene reduced nitrobenzenes to the corresponding anilines in the presence of Pd–carbon,[3] and the mechanism of the reduction was hardly discussed.

During the course of the systematic study of transfer hydrogenations, we found that aromatic nitro compounds were reduced to the corresponding amines in the presence of noble metal salts under mild reaction conditions. So we undertook this study to enlarge the scope of the transfer hydrogenation of nitroaryls and to discuss the mechanism of the reaction.

Results and Discussion

Catalytic Activity. In the reaction system in which indoline (1.5 mol l.$^{-1}$), nitrobenzene (0.5 mol l.$^{-1}$), and a soluble catalyst (0.08 mol l.$^{-1}$) or a metallic palladium catalyst (20 g/l.) were heated in toluene at 80 °C for 4 h, the activity of several catalysts was examined. Although some of the noble metal

Table I. Rate of Reduction of Monosubstituted Nitrobenzenes[a]

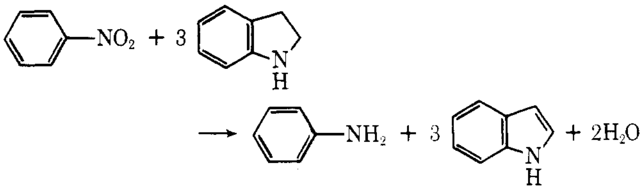
Registry no.	Hydrogen acceptor	Rate, mol l.$^{-1}$ min^{-1}
100-00-5	*p*-Nitrochlorobenzene	33.9×10^{-4}
100-19-6	*p*-Nitroacetophenone	32.0×10^{-4}
98-95-3	Nitrobenzene	23.4×10^{-4}
88-73-3	*o*-Nitrochlorobenzene	11.0×10^{-4}
121-73-3	*m*-Nitrochlorobenzene	6.7×10^{-4}
554-84-7	*m*-Nitrophenol	6.3×10^{-4}
100-02-7	*p*-Nitrophenol	5.2×10^{-4}
100-17-4	*p*-Nitroanisole	5.0×10^{-4}
99-99-0	*p*-Nitrotoluene	4.3×10^{-4}
100-01-6	*p*-Nitroaniline	4.2×10^{-4}
99-08-1	*m*-Nitrotoluene	4.0×10^{-4}
88-72-2	*o*-Nitrotoluene	3.1×10^{-4}
88-75-5	*o*-Nitrophenol	1.7×10^{-4}

[a] $RhCl_3 \cdot 3H_2O$ (0.08 mol l.$^{-1}$), indoline (1.5 mol l.$^{-1}$), and the hydrogen acceptor (0.5 mol l.$^{-1}$) were heated in dioxane at 80 °C.

salts scarcely dissolved in toluene at room temperature, they dissolved in the solvent at the reaction temperature in the presence of the reactants. In these conditions, the amount of metallic palladium in 5% Pd–carbon, 50% Pd–asbestos, or Pd black is about 0.12, 1.2, or 2.3 times as much as that in palladium salts, respectively. Under this condition, $RuCl_3 \cdot H_2O$ (88%) and $RhCl_3 \cdot 3H_2O$ (82%) showed high catalytic activity. $PdBr_2$ (50%) and $PdCl_2$ (20%) showed moderate and $ReCl_5$ (5%), $(NH_4)_2PdCl_4$ (3%), and K_2PtCl_4 (2%) low catalytic activity. Here, the percentages shown in parentheses are the yield of aniline. K_2PtCl_6, $FeCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $RhCl(PPh_3)_3$, $RhH(PPh_3)_4$, $RuCl_2(PPh_3)_3$, and $RuH_2(PPh_3)_4$ hardly catalyzed the reduction. Pd black, Pd–carbon, and Pd–asbestos gave yields of 52, 18, and 6%, respectively. A rather good reproducibility of the results was confirmed. It is noteworthy that the triphenylphosphine complexes which exhibited high catalytic activity in the transfer hydrogenation of olefins and carbonyl compounds[4–7] showed no activity. Perhaps this fact is explained by the inference that nitrobenzene, which is strongly polarized,[8] has strong coordinating power and several nitrobenzene molecules occupy the coordination sites of the catalysts to make the coordination of indoline difficult. In any experiments described hereafter, $RhCl_3 \cdot 3H_2O$ was used as a catalyst.

Hydrogen Donors. We have previously reported that ethers,[4,7] amines,[5] alcohols,[6] and hydrocarbons[7] donated their hydrogen atoms to olefins and aldehydes in the presence of phosphine complexes or Pd–carbon. When the reduction of nitrobenzene was carried out in toluene at 120 °C for 4 h in the presence of $RhCl_3 \cdot 3H_2O$, indoline was found to have an excellent hydrogen donating ability (97%). Secondary cyclic amines, such as tetrahydroquinoline (57%), 3-pyrroline (45%), piperidine (28%), and pyrrolidine (23%), functioned as fair hydrogen donors. Here, the percentages shown in parentheses are the yield of aniline. In the reaction of indoline and tetrahydroquinoline the stoichiometric amounts of indole and quinoline were detected, respectively. *N*-Methylpiperidine, *N*-methylpyrrolidine, 2,5-dihydrofuran, tetralin, and cyclohexene hardly showed hydrogen donating ability. Tri-*n*-propylamine, cyclohexylamine, 2-propanol, methanol, cyclohexanol, 1-phenylethanol, dioxane, tetrahydrofuran, and indan showed no hydrogen donating ability. Since nitrobenzene seems to have strong coordinating power by the high degree of N–O bond polarization,[8] the hydrogen donors with strong coordinating power may be effective for the reduction of nitrobenzene. At least partly, the higher hydrogen donating ability of secondary cyclic amines is explained by this inference.

When indoline (1.5 mol l.$^{-1}$), nitrobenzene (0.5 mol l.$^{-1}$), and $RhCl_3 \cdot 3H_2O$ (0.08 mol l.$^{-1}$) were heated in toluene at 80 °C for 4 h, aniline was obtained in 82% yield (0.41 mol l.$^{-1}$) along with the dehydrogenation product, indole (1.30 mol l.$^{-1}$), and survived indoline (0.19 mol l.$^{-1}$) and nitrobenzene (0.09 mol l.$^{-1}$) also were detected in the reaction mixture. This result is summarized as follows. (1) The amount of indole was equal to the theoretical one within experimental errors, because 1.31 mol l.$^{-1}$ of hydrogen is needed to form 0.41 mol l.$^{-1}$ of aniline and to reduce 0.08 mol l.$^{-1}$ of a Rh(III) species to a Rh(I) species. (2) The total amount of indoline and indole was nearly equal to the amount of the charged indoline. (3) The total amount of aniline and nitrobenzene was equal to the amount of the charged nitrobenzene. Other products, such as azo and azoxy compounds, were not detected by GLC and TLC analysis. These results show that the following reaction proceeded without remarkable side reactions.



Reaction Solvents. When ethanol, *N,N*-dimethylformamide, ethyl acetate, benzene, dioxane, chlorobenzene, toluene, and methanol were used as solvents, the yield of aniline was not so varied. This fact may be explained by the presumption that indoline and nitrobenzene coordinate rather strongly on catalytic species. However, the reduction proceeded rather slower in *N,N*-dimethylacetamide and much slower in dimethyl sulfoxide and benzonitrile. These compounds may coordinate so strongly as to prevent the coordination of the hydrogen donor. When the reaction was carried out in water, a black, tarry material was formed and no aniline was detected.

Effect of Additives. The addition of sodium borohydride to the reaction system promoted the reduction of nitrobenzene. The hydride donated the hydrogen atoms catalytically, because it could not reduce nitrobenzene without a catalyst. Therefore, sodium borohydride was found to be an excellent hydrogen donor. Water, which is one of the products, and anhydrous sodium sulfate, which is a dehydrating agent, did not affect the reduction. The addition of hydrochloric acid moderately retarded the reduction. Perhaps, the acid deactivates the hydrogen donor by salt formation and the catalyst by coordination. Although the removal of hydrogen chloride seems to be necessary in order to activate $RhCl_3$ as described later, the addition of the amines having no hydrogen donating ability, such as *n*-propylamine, tri-*n*-octylamine, *N,N*-dimethylaniline, and pyridine, decreased the yield of aniline. The addition of triphenylphosphine and triphenyl phosphite also retarded the reaction. These inhibitors coordinate to the metal and make the coordination of indoline difficult. The addition of potassium hydroxide, which has been reported to promote the reduction of nitro compounds by molecular hydrogen,[2b] inhibited the transfer hydrogenation completely, because the addition caused the precipitation of metallic rhodium.

Substituent Effect. Initial rates of the reduction of monosubstituted nitrobenzenes were measured in dioxane, which has higher dissolving ability than toluene (Table I). Roughly speaking, the substances having electron-withdrawing substituents were reduced more rapidly than those having electron-donating ones.[1c] In order to interpret this result, the coordination ability of nitrobenzenes was evaluated. The visible spectrum of the methanol solution of $RhCl_3 \cdot 3H_2O$ showed an absorption peak at 510 nm (ϵ 160) and the strength of the peak decreased gradually after the addition of nitro-

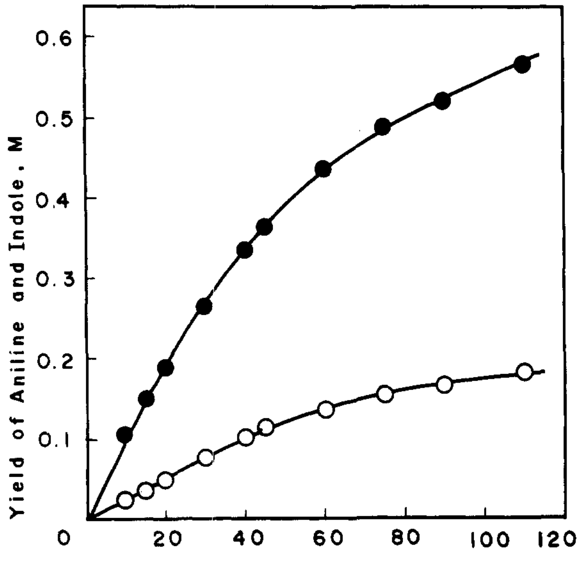


Figure 1. Plot of the yield of aniline and indole vs. reaction time. $RhCl_3 \cdot 3H_2O$ (0.04 mol $l.^{-1}$), indoline (1.5 mol $l.^{-1}$), and nitrobenzene (0.5 mol $l.^{-1}$) were heated in methanol at 70 °C. (○), aniline; (●), indole.

benzenes. The nitrobenzenes having p-Cl, p-$COCH_3$, H, p-CH_3, or p-OCH_3 as a substituent showed almost the same initial rate of the disappearance of the peak and nearly equal final strength of the peak. This result suggests that the coordinating powers of nitrobenzenes were not so different. The substituent effect in the reduction of nitrobenzenes might be caused by the ease of the hydrogen transfer from a metal hydride intermediate to the coordinated nitrobenzenes and/or by the ability of the complexes coordinated by nitrobenzenes to accept hydrogen atoms from indoline.

Aliphatic nitro compounds were not reduced under these reaction conditions. Partly reduced derivatives, nitrosobenzene and phenylhydroxylamine, were reduced to aniline much faster under the condition in Table I with rates of 1.26×10^{-2} and 1.23×10^{-2} mol $l.^{-1}$ min^{-1}, respectively. Hydrazobenzene and azobenzene could be reduced to aniline under the same condition with rates of 8.5×10^{-3} and 5.9×10^{-3} mol $l.^{-1}$ min^{-1}, respectively.

Kinetic Study

A kinetic study was carried out using methanol as solvent. Figure 1 shows an example of the yield of aniline and indole against time plots, and indicates that the reproducibility of the reaction was fairly good because the data shown in the figure were obtained by different runs (see Experimental Section). The yield of aniline was proportional to reaction time until about 0.10 mol (20%) and the initial rate of the reduction of nitrobenzene was derived from the linear part. The rate showed the first-order dependence on the concentration of the catalyst and that of indoline (Figure 2). The initial rate decreased with the increase of the concentration of nitrobenzene, and the reciprocal of the rate against the concentration of nitrobenzene was linear with a positive intercept on the y axis (Figure 3). The data in Figure 3 may be accommodated by the relationship

$$1\Big/\frac{d[PhNH_2]}{dt} = a[PhNO_2] + b \qquad (1)$$

where a and b are constants.

Based on the results described above, the rate of the reduction can be described by the expression

$$\frac{d[PhNH_2]}{dt} = k\frac{[Rh]_0[\text{indoline}]}{1 + K[PhNO_2]} \qquad (2)$$

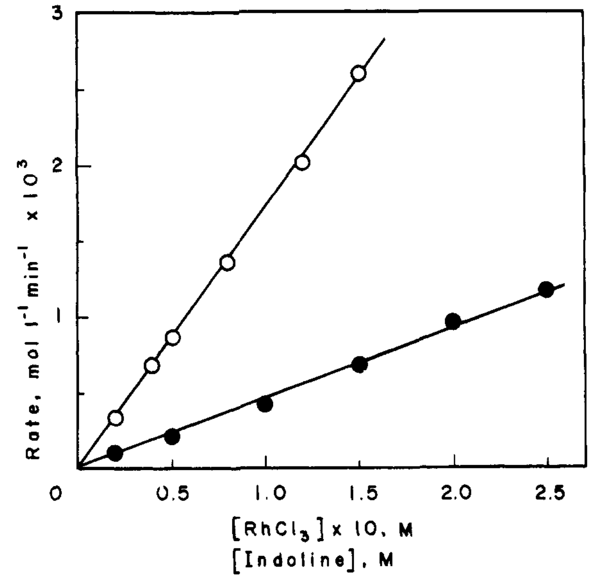


Figure 2. Dependence of rate of reduction of nitrobenzene (0.5 mol $l.^{-1}$) on the concentration of the catalyst (○) (1.5 mol $l.^{-1}$ indoline) and indoline (●) (0.04 mol $l.^{-1}$ $RhCl_3 \cdot 3H_2O$) in methanol at 60 °C.

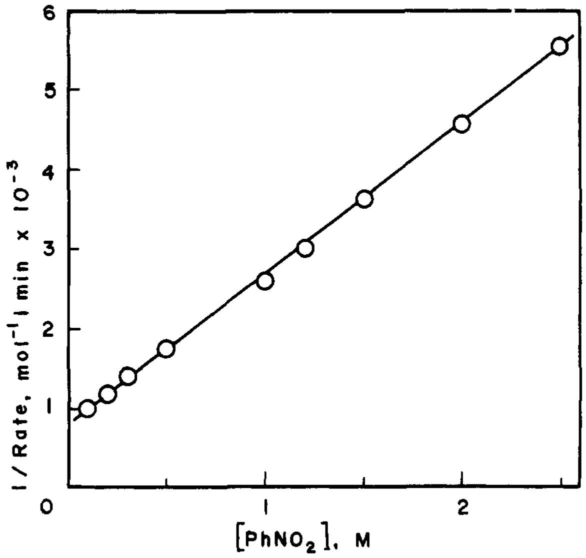


Figure 3. Dependence of rate of reduction of nitrobenzene on the concentration of nitrobenzene. $RhCl_3 \cdot 3H_2O$ (0.04 mol $l.^{-1}$), indoline (1.5 mol $l.^{-1}$), and nitrobenzene were heated in methanol at 60 °C.

where the rate constant, k, had the value of 0.08 mol^{-1} l. min^{-1}, and the constant, K, had that of 1.5 mol^{-1} l. Since the dimension of K does not contain time, K is inferred to be an equilibrium constant or a ratio of rate constants.

Initial rates were measured at temperatures ranging from 40 to 100 °C and the Arrhenius plot showed a good linear relationship, indicating that the kinetics of the system and are not so complicated. From the plot, the activation energy of 14.4 kcal mol^{-1} was obtained.

Discussion of Mechanism

It has been reported that $RhCl_3$, which was used as a catalyst, is reduced to a Rh(I) species in the reduction of unsaturated compounds by molecular hydrogen.[9] In our system too, Rh(I) species are assumed to be active catalytic species by the following observations: (1) Indoline was dehydrogenated to indole by heating with $RhCl_3$ in the absence of a hydrogen acceptor and the reaction mixture did not show the absorption peak at 510 nm which may be assignable to a Rh(III) species, while the peak remained unchanged in the mixture which had not been heated. (2) The amount of indole in a reaction mixture was larger than the one calculated from the yield of aniline and nearly equalled the one needed to reduce both nitrobenzene and $RhCl_3$.

We should like to propose the following reaction process for the transfer hydrogenation of nitrobenzene.

$$Rh^{III}Cl_3 + \text{indoline} \rightarrow Rh^{I}Cl + \text{indole} + 2HCl \quad (3)$$

$$Rh^{I}Cl + PhNO_2 \rightarrow Rh^{I}Cl(PhNO_2) \quad (4)$$

$$Rh^{I}Cl(PhNO_2) + 3\ \text{indoline} \rightarrow Rh^{I}Cl + PhNH_2 + 3\ \text{indole} + 2H_2O \quad (5)$$

According to this suggestion, $RhCl_3$ is activated to a Rh(I) species by indoline (eq 3), nitrobenzene coordinates to the Rh(I) species (eq 4), and then the coordinated nitrobenzene is reduced to aniline by the hydrogen donor (eq 5). As described before, the coordination of nitrobenzenes to $RhCl_3$ was confirmed by the spectroscopic study.

$$Rh^{III}Cl_3 + PhNO_2 \overset{K'}{\rightleftarrows} Rh^{III}Cl_3(PhNO_2) \quad (6)$$

The rate expression, eq 2, suggests that this step is not involved in the catalytic cycle of the reduction and K' in eq 6 corresponds to K in eq 2, because the term $[PhNO_2]$ appears only in the denominator of eq 2. Further, eq 2 indicates that the coordination of nitrobenzenes to $RhCl_3$ and Rh(I) species occurs in parallel and that the formation of Rh(I) species from the Rh(III) species in eq 3 is depressed by the coordination of nitrobenzene to $RhCl_3$.

In the process of the hydrogen transfer shown in eq 5, 3 mol of indoline is necessary for the reduction of 1 mol of nitrobenzene. Therefore, three hydrogen transfer steps from indoline will be involved, as shown in Scheme I.

Scheme I

$$PhNO_2 \xrightarrow[\substack{-\text{indole}\\ -H_2O}]{\text{indoline}} PhNO \xrightarrow[-\text{indole}]{\text{indoline}} PhNHOH \xrightarrow[\substack{-\text{indole}\\ -H_2O}]{\text{indoline}} PhNH_2$$

In the reduction of nitrobenzene, nitrosobenzene was detected, but phenylhydroxylamine was not. Since nitrosobenzene and phenylhydroxylamine were reduced to aniline about five times as fast as nitrosobenzene, the deoxygenation of nitrobenzene to nitrosobenzene is considered to be the rate-determining step.

Experimental Section

Materials. Rhodium trichloride, ruthenium trichloride, palladium bromide, palladium chloride, rhenium pentachloride, ammonium palladous chloride, potassium chloroplatinate, palladium black, palladium carbon, and palladium asbestos were purchased and used without purification. Amines, alcohols, ethers, and hydrocarbons were purified by distillation and dried by the usual methods. Nitrobenzene, *p*- and *m*-nitrotoluene, and *o*- and *m*-nitrochlorobenzene were purified by distillation. Other nitrobenzenes, nitrosobenzene, azobenzene, and hydrazobenzene were purified by recrystallization. Phenylhydroxylamine was synthesized by the method reported in the literature.[10]

An Example of Transfer Hydrogenation. Nitrobenzene (30.8 mg, 0.25 mmol), indoline (89.3 mg, 0.75 mmol), and $RhCl_3 \cdot 3H_2O$ (10.5 mg, 0.04 mmol) were put into a Pyrex tube which had been sealed at one side. Into the mixture, toluene was added and the total volume of the solution was made 0.5 ml. The tube was sealed under vacuum with two freeze–pump–thaw cycles at 10^{-3} Torr on a vacuum line with liquid nitrogen bath. The sealed tube was heated for 4 h in a polyethylene glycol bath kept at 80 ± 1 °C. To determine the amount of aniline formed, the reaction mixture was submitted to GLC analysis which was performed at 130 °C using 2 m × 6 mm stainless steel column packed with 15% of Silicone DC 11 on Diasolid L and 25 μl of benzene as an internal standard. The amount of indole and indoline was measured by the use of a 2 m × 6 mm column packed with 10% diethylene glycol succinate on Diasolid L and of dibenzyl ether as an internal standard. Then the reaction mixture was treated by TLC technique in order to isolate the produced amines. The isolated products were identified by comparison with authentic samples in the IR spectra.

The other transfer hydrogenations were carried out in a similar way. However, in the reactions catalyzed by the heterogeneous catalysts the sealed tubes were heated with continuous oscillation.

An example of Kinetic Runs. Five samples, prepared by the method described above, were heated in a polyethylene glycol bath kept at 60 ± 1 °C for 10, 20, 30, 45, and 60 min, respectively. The reaction mixtures were submitted to GLC analysis.

Registry No.—Aniline, 62-53-3; indole, 120-72-9; indoline, 496-15-1; $RhCl_3$, 10049-07-7.

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