Studies on Selective Preparation of Aromatic Compounds. 13. Formation of Benzquinhydrone Type Complexes from 2-*tert*-Butylhalophenols in Alkaline Solution and Their Reduction with Zinc Powder in Acetic Acid Affording 4,4'-Dihydroxybiphenyls

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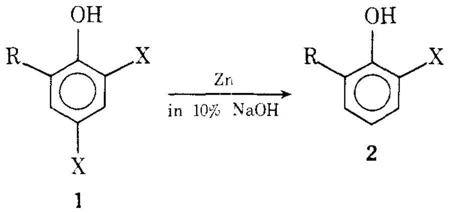
Dark violet compounds (**3a–d**) were formed in good yields when a solution of 2-*tert*-butylhalophenols (**1e–h**) in 10% sodium hydroxide was warmed at 80 °C. However, 2,6-di-*tert*-butyl-4-bromophenol (**1i**) afforded 3,5,3',5'-tetra-*tert*-butyldiphenoquinone (**4**) in the Claisen alkaline reagent. Compounds **3a–d** are quinhydrone type charge transfer complexes based on spectral and elemental data as well as their chemical conversion to 4,4'-dihydroxybiphenyls (**5a–d**) on reduction with zinc powder in acetic acid. Mechanisms for the formation of **3** are also discussed in this paper.

It has been previously reported that[1] some halophenols (**1**) were easily reduced with zinc powder in 10% sodium hydroxide solution to afford the reductive dehalogenated compounds (**2**) which were mainly *o*-halophenols, that is, the *p*-bromo or -iodo group was selectively reduced to give **2**. It was also found that in the case of 2-*tert*-butyl-4,6-dihalophenol (R = *t*-Bu) the rapid addition of zinc powder to an alkaline solution of **1** or addition of **1** to a suspension of zinc powder in alkaline solution was necessary to avoid the formation of dark violet compounds (**3**).



1 **2**

+ dark violet compound (1)
3

In order to clarify the structure and the mechanism for the formation of **3**, several halophenols were treated with 10% sodium hydroxide or the Claisen alkaline reagent.[2]

Results and Discussion

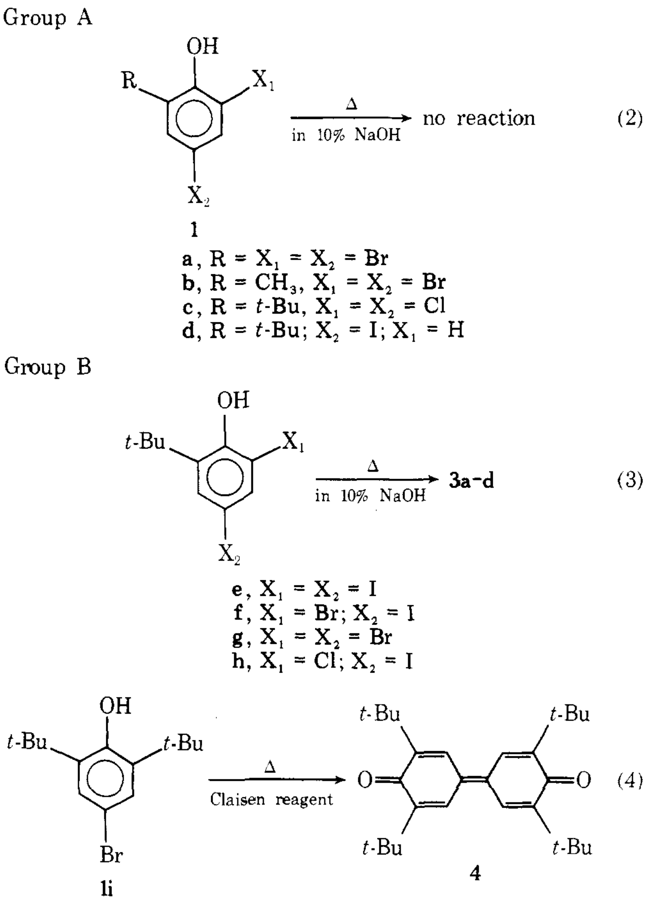
Treatments of 2,4,6-tribromo- (**1a**), 2,4-dibromo-6-methyl- (**1b**), 2,4-dichloro-6-*tert*-butyl- (**1c**), 2-*tert*-butyl-4-iodo- (**1d**), 2-chloro-6-*tert*-butyl- (**1e**), 2,4-dibromo-6-*tert*-butyl- (**1f**), 2-bromo-6-*tert*-butyl-4-iodo- (**1g**), 2-*tert*-butyl-4,6-dibromo- (**1h**), and 2,6-di-*tert*-butyl-4-bromophenol (**1i**) with 10% sodium hydroxide or the Claisen alkaline reagent[2] were carried out at 80 °C and the results are summarized in Table I and Scheme I. The latter condition was only used in the case of **1i**, which was not soluble in 10% sodium hydroxide solution. These reactions took place at room temperature, although the reaction time was longer than at 80 °C.

Table I. Treatment of 1 with Alkaline Solution at 80 °C[a]

Run	Substance	Time, min	Product (%)
1	**1a**	60	No reaction
2	**1b**	60	No reaction
3	**1c**	60	No reaction
4	**1d**	60	No reaction
5	**1e**	5	**3a** (99.7)
6	**1f**	5	**3b** (91.6)
7	**1g**	15	**3c** (99.5)
8	**1h**	5	**3d** (85.7)
9[b]	**1i**	60	**4** (95)

[a] The 10% sodium hydroxide solution was used unless otherwise indicated. [b] The Claisen alkaline solution was used.

Scheme I



1

a, R = X_1 = X_2 = Br
b, R = CH_3, X_1 = X_2 = Br
c, R = *t*-Bu, X_1 = X_2 = Cl
d, R = *t*-Bu; X_2 = I; X_1 = H

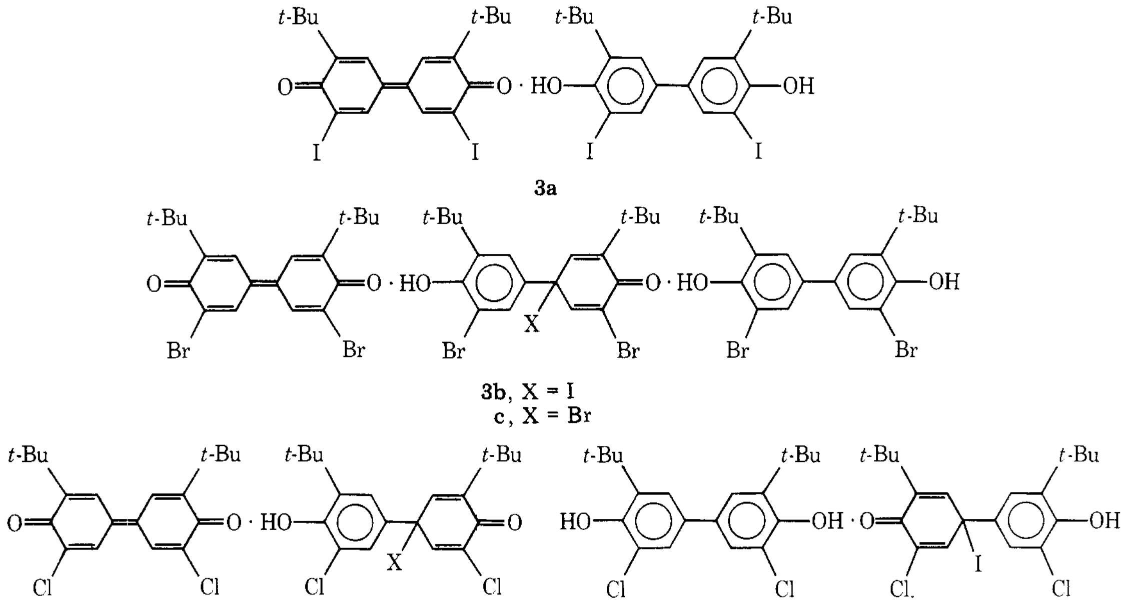
e, X_1 = X_2 = I
f, X_1 = Br; X_2 = I
g, X_1 = X_2 = Br
h, X_1 = Cl; X_2 = I

1i **4**

The data of Table I show that the phenols (**1**) can be classified into three groups (A, B, and C) as shown in Scheme I; group A (**1a–d**) did not react, group B (**1e–h**) afforded good yields of **3a–d**, respectively, group C (compound **1e**) gave 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenoquinone (**4**), a product formed in the oxidation of 2,6-di-*tert*-butylphenol.[3–6]

Formation of **3** from **1** in alkaline solution requires the following three factors: (1) the alkyl group ortho to the hydroxy group should be *tert*-butyl but not methyl, (2) X_2 should be bromo or iodo but not chloro group, and (3) X_1 should be chloro, bromo, or iodo group but not hydrogen.

Scheme II



3a

3b, X = I
c, X = Br

3d$_1$ **3d$_2$**

Table II. IR Spectra of 3[a]

Run	Substance	$\nu_{C=O}$, cm^{-1}	ν_{OH}, cm^{-1}
1	**3a**	1610	3440
2	**3b**	1620	3460
3	**3c**	1620	3460
4	**3d**	1620	3420

[a] IR spectra were measured as KBr pellets.

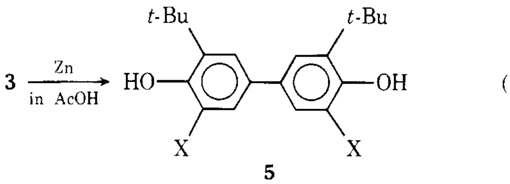
Table III. Reduction of 3 with Zinc Powder in AcOH at 20 °C

Run	3	Time, min	Product (%)
1	**a**	5	**5a** (75.5)
2[a]	**a**	60	**5d** (63)
3	**b**	30	**5b** (85.9)
4	**c**	30	**5b** (87.6)
5	**d**	30	**5c** (86)

[a] Reaction temperature 100 °C.

The infrared spectra of **3** are summarized in Table II. As is shown in Table II, all of **3** have quinoidal carbonyl and phenolic hydroxy groups. The ultraviolet spectra of **3** show strong absorptions in the visible region (see Experimental Section).

When compounds **3a–d** were treated with zinc powder in acetic acid, the corresponding 4,4′-dihydroxybiphenyls (**5**)



(5)

5

a, X = I
b, X = Br
c, X = Cl
d, X = H

were obtained in good yield (Table III).

It should be noted that the reduction of **3b** and **3c** afforded the same product, 3,3′-dibromo-5,5′-di-*tert*-butyl-4,4′-dihydroxybiphenyl (**5b**). The reduction of **3a** at 100 °C gave 3,3′-di-*tert*-butyl-4,4′-dihydroxybiphenyl (**5d**) but not 3,3′-di-*tert*-butyl-5,5′-diiodo-4,4′-dihydroxybiphenyl (**5a**), which was obtained by the reduction of **3a** at 20 °C for 5 min. The above result suggests that the iodo group of **5a** is easily reduced to afford **5d**. Indeed, **5d** was obtained in good yield by the reduction of **5a** at 100 °C with zinc powder in acetic acid.

However, in contrast to results with **5a**, compounds **5b** and **5c** did not yield **5d** under the same conditions used to reduce **5a**.

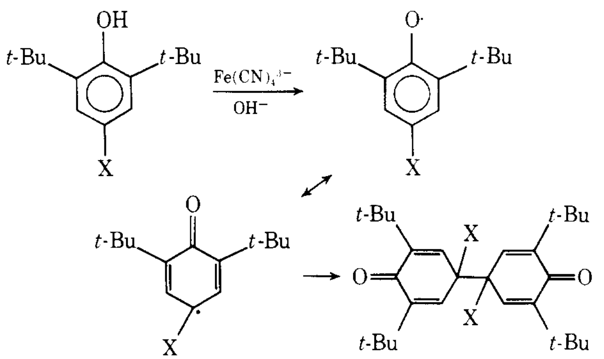
$$\mathbf{5a} \xrightarrow[\text{in AcOH}]{\text{Zn}} \mathbf{5d} \qquad (6)$$

$$\mathbf{5b\text{–}c} \overset{\text{Zn}}{\underset{\text{in AcOH}}{\not\longrightarrow}} \mathbf{5d} \qquad (7)$$

Compounds **3a** and **5a** might be good starting compounds in the preparation of **5d**, a compound which could not be prepared in the usual manner.[7]

Based on the results described above and the spectral data as well as elemental analyses of **3**, compounds **3a–d** are proposed to be quinhydrone type charge transfer complexes (Scheme II).

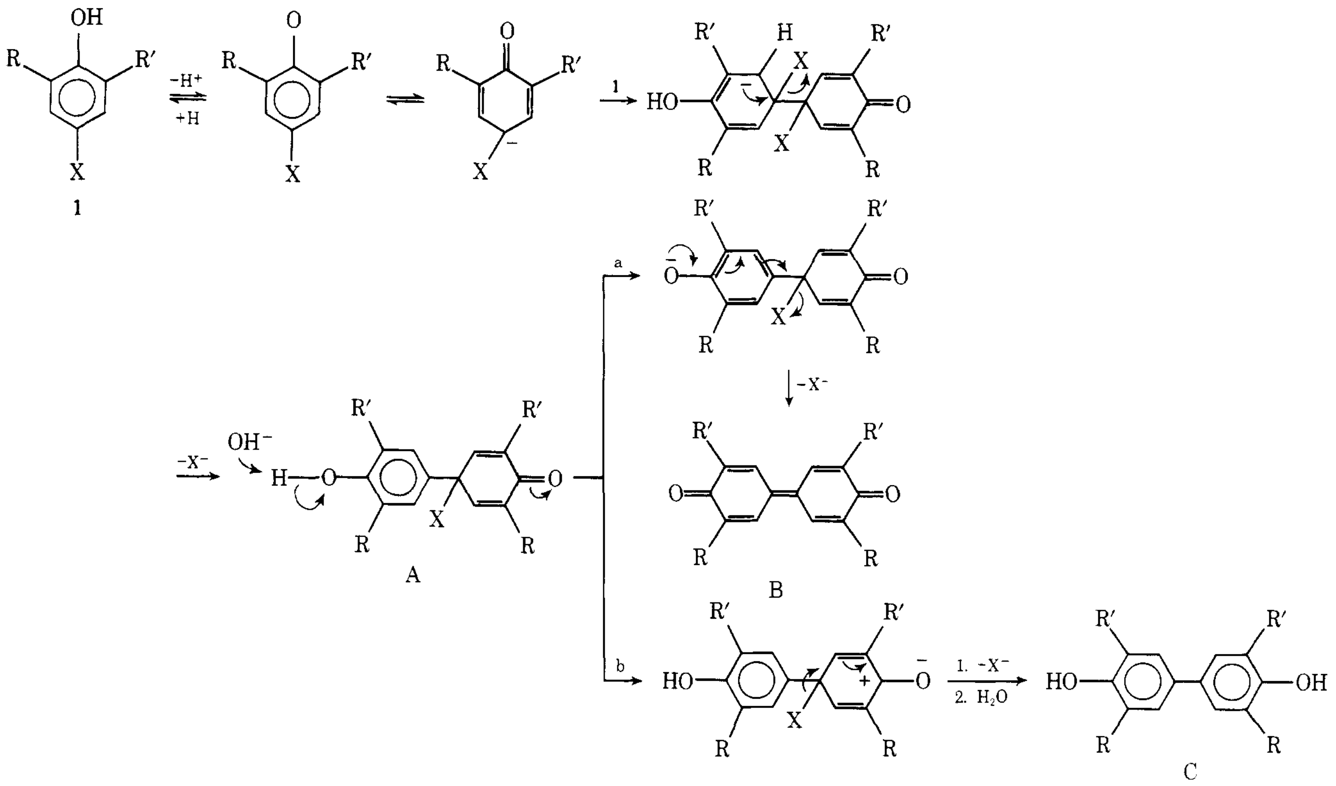
The ^{13}C NMR spectrum of **3c** shows a signal at 37.8 ppm which can be assigned to an sp^3 carbon atom bonded to a bromine atom. This signal could not be observed in the ^{13}C NMR spectrum of **3a**. These results also support the proposed structure of **3**. Unfortunately, it could not be determined whether structure **3d$_1$** or **3d$_2$** is correct based on the available data. The conversion of **1** to **3** took place even under a nitrogen atmosphere. Recently the formation of 1,1′-dihalo-3,5,3′,5′-tetra-*tert*-butyl-2,5,2′,5′-biscyclohexadien-4,4′-one (**6**) in the



(8)

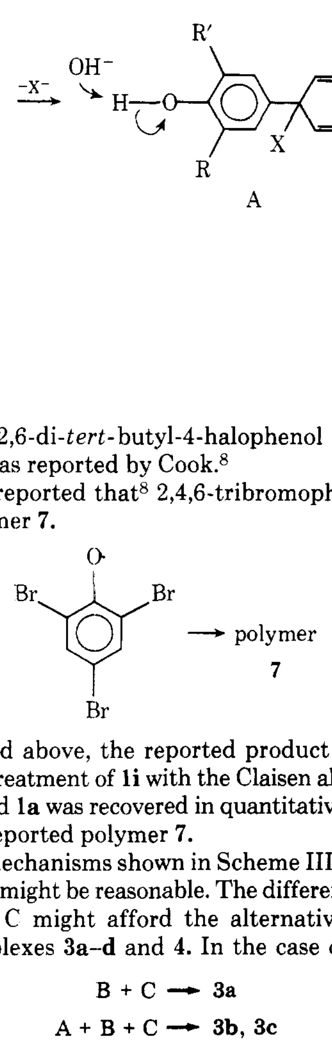
6

Scheme III



oxidation of 2,6-di-*tert*-butyl-4-halophenol with alkaline ferricyanide was reported by Cook.[8]

It was also reported that[8] 2,4,6-tribromophenoxy radical afforded polymer **7**.



(9)

As described above, the reported product **6** was not obtained in the treatment of **1i** with the Claisen alkaline reagent. Also compound **1a** was recovered in quantitative yield and did not give the reported polymer **7**.

The ionic mechanisms shown in Scheme III for the formation of **3** and **4** might be reasonable. The different combination of A, B, and C might afford the alternative type charge transfer complexes **3a–d** and **4**. In the case of **4**, the steric

$$\mathrm{B} + \mathrm{C} \longrightarrow \mathbf{3a} \qquad (10)$$

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \longrightarrow \mathbf{3b}, \mathbf{3c} \qquad (11)$$

$$\left.\begin{matrix} \mathrm{A} + \mathrm{B} \\ \text{or} \\ \mathrm{A} + \mathrm{C} \end{matrix}\right\} \longrightarrow \mathbf{3d} \qquad (12)$$

$$\mathrm{B} \longrightarrow \mathbf{4} \qquad (13)$$

hindrance of two *tert*-butyl groups might preclude such complexation and yield only B (**4**).

Experimental Section

All melting points are uncorrected. IR spectra were measured as KBr pellets on a Nippon Bunko IR-S spectrophotometer and NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer using Me_4Si as an internal reference.

Treatment of 2,4,6-Tribromo- (1a),[8] 2,4-Dibromo-6-methyl- (1b),[9] 2,4-Dichloro-6-*tert*-butyl- (1c),[10] and 2-*tert*-Butyl-4-iodophenol (1d)[1] with 10% Sodium Hydroxide. After a solution of 5 g of **1** (**1a–d**) in 50 ml of 10% sodium hydroxide was heated at 80 °C for 60 min, the reaction mixture was acidified with 10% hydrochloric acid and extracted with benzene. The extract was dried over sodium sulfate and evaporated in vacuo to afford the starting material **1** in almost quantitative yields, respectively.

Formation of 3a from 2-*tert*-Butyl-4,6-diiodophenol (1e). After a solution of 5 g (12.5 mmol) of **1e** in 50 ml of 10% sodium hydroxide was heated at 80 °C for 5 min, the precipitated dark violet product was collected by filtration and washed with a large amount of water and then with a small amount of ether to afford 3.4 g (99.7%) of **3a**: mp 122–140 °C dec; IR (KBr) 3440 (OH), 1610 cm^{-1} (C=O); UV λ_{max} (EtOH) 322 nm (log ϵ 4.73), 255 (4.36), 290 (4.23), 428 (4.71), 444 (4.65), 475 (4.53).

Anal. Calcd for $C_{40}H_{46}O_4I_4$: C, 43.74; H, 4.22. Found: C, 43.48; H, 4.20.

Formation of 3b from 2-Bromo-6-*tert*-butyl-4-iodophenol (1f). When a solution of 3.55 g (10 mmol) of **1f**[1] in 50 ml of 10% sodium hydroxide was heated at 80 °C for 5 min, similarly 2.4 g (91.6%) of **3b** was isolated: mp 110–135 °C dec; IR (KBr) 3460 (OH), 1620 cm^{-1} (C=O); UV λ_{max} (EtOH) 220 nm (log ϵ 4.90), 240 (4.62), 270 (4.56), 417.5 (5.09), 428 (5.12), 435 (5.11).

Anal. Calcd for $C_{60}H_{69}O_6Br_6I$: C, 48.28; H, 4.66. Found: C, 48.32; H, 4.49.

Formation of 3c from 2,4-Dibromo-6-*tert*-butylphenol (1g). Similarly 2.5 g (8 mmol) of **1g**[11] was treated at 80 °C for 15 min and worked up as described above to afford 1.95 g (99.5%) of dark brown product (**3c**): mp 85–100 °C dec; IR (KBr) 3460 (OH), 1620 cm^{-1} (C=O); UV λ_{max} (EtOH) 220 nm (log ϵ 4.95), 240 (4.79), 270 (4.55), 417.5 (4.99), 428 (5.04), 435 (5.21).

Anal. Calcd for $C_{60}H_{69}O_6Br_7$: C, 49.85; H, 4.81. Found: C, 49.98; H, 4.61.

Formation of 3d from 2-Chloro-6-*tert*-butyl-4-iodophenol (1h). Similarly 0.5 g (1.6 mmol) of **1h**[1] was treated at 80 °C for 5 min and worked up as described above to afford 0.3 g (85.7%) of **3d**: mp 90–105 °C dec; IR (KBr) 3420 (OH), 1620 cm^{-1} (C=O); UV λ_{max} (EtOH) 220 nm (log ϵ 4.75), 240 (4.41), 260 (4.27), 270 (4.24), 280 (4.22), 412 (4.79), 426 (4.85), 432 (4.74).

Anal. Calcd for $C_{40}H_{45}O_4Cl_4I$: C, 55.96; H, 5.28. Calcd for $C_{40}H_{47}O_4Cl_4I$: C, 55.83; H, 5.51. Found: C, 56.51; H, 5.32.

Reduction of 3a. A. At 20 °C. To a solution of 2 g (1.8 mmol) of **3a** in 40 ml of acetic acid was added at 20 °C 4 g of zinc powder. The reduction mixture was stirred for 5 min and the unreacted zinc powder was filtered off. To the filtrate was added 80 ml of water, affording 1.56 g (75.5%) of **5a**, mp 85–89 °C dec, as a colorless, crystalline powder ($AcOH-H_2O$): IR (KBr) 3550 (shoulder), 3480 cm^{-1} (OH); NMR ($CHCl_3$) δ 1.45 [18 H, s, $(CH_3)_3$], 5.52 (2 H, s, OH), 7.35 (2 H, d, J = 2.2 Hz), 7.64 (2 H, d, J = 2.2 Hz, aromatic protons).

Anal. Calcd for $C_{20}H_{24}O_2I_2$: C, 43.66; H, 4.40. Found: C, 43.46; H, 4.60.

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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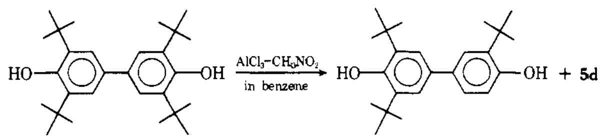

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Transfer Hydrogenation and Transfer Hydrogenolysis. 13. Hydrogen Transfer from Cyclic Amines to Aromatic Nitro Compounds Catalyzed by Noble Metal Salts

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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