reagent grade quality. Aqueous solutions containing the metal salts were deoxygenated by bubbling argon through 1 l. of the solution for 1 h. The saturation was enhanced by frequent shaking. The aromatic compound was added and the solution was shaken to enhance the saturation. Then $Na_2S_2O_8$ was added at once and the solution was shaken and left to react for different times. All solutions were homogeneous and the reactions were carried out at room temperature. The solutions were extracted once with 200 ml of ether and four times with 100 ml of ether. The ether extracts were dried over Na_2SO_4, concentrated to 10 ml, and analyzed by vapor phase chromatography. The analytical procedure has been described in detail in previous publications.[4-6]

Registry No.—Toluene, 108-88-3; peroxydisulfate, 15092-81-6; fluorobenzene, 462-06-6; anisole, 100-66-3; nitrobenzene, 98-95-3; benzonitrile, 100-47-0; $K_4Fe(CN)_6$, 13943-58-3; $K_3Fe(CN)_6$, 13746-66-2; $Fe(NH_4)_2(SO_4)_2$, 10045-89-3; $Fe(NH_4)(SO_4)_2$, 10138-04-2; $CuSO_4$, 10124-44-4.

References and Notes

(1) This paper was prepared in connection with work under Contract E-(40-1)-1833 with the U.S. Energy Research and Development Administration (ERDA). ERDA retains a nonexclusive, royalty-free license in and to any copyright covering this paper, with the right to authorize others to reproduce all or any part of the copyrighted paper.
(2) L. M. Dorfman, I. A. Taub, and R. E. Buhler, *J. Chem. Phys.*, **36**, 3051 (1962).
(3) J. H. Baxendale and D. Smithies, *J. Chem. Soc.*, 799 (1959).
(4) M. K. Eberhardt, *J. Phys. Chem.*, **79**, 1913 (1975).
(5) M. K. Eberhardt and M. I. Martinez, *J. Phys. Chem.*, **79**, 1917 (1975).
(6) M. K. Eberhardt, *J. Phys. Chem.*, accepted for publication.
(7) C. Walling and D. M. Camaioni, *J. Am. Chem. Soc.*, **97**, 1603 (1975).
(8) For a detailed description of this method see J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Methods", McGraw-Hill, New York, N.Y., 1970. The computer program was obtained from the Quantum Chemistry Program Exchange, Bloomington, Ind., and was written by A. Dobosh.
(9) R. O. C. Norman, P. M. Storey, and P. R. West, *J. Chem Soc. B*, 1087 (1970).
(10) R. O. C. Norman, P. M. Storey, and P. R. West, *J. Chem. Soc. B*, 1099 (1970).
(11) M. E. Snook and G. A. Hamilton, *J. Am. Chem. Soc.*, **96**, 860 (1974).
(12) A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *Chem. Commun.*, 964 (1971); *Proc. R. Soc. London, Ser. A*, **332**, 151 (1973); *J. Chem. Soc., Perkin Trans. 2*, 630 (1973).
(13) A. Ledwith and P. J. Russell, *J. Chem. Soc., Chem. Commun.*, 291, 959 (1974).
(14) P. O'Neill, S. Steenken, and D. Schulte-Frohlinde, *J. Phys. Chem.*, **79**, 2773 (1975).
(15 P. Neta, H. Zemel, V. Madhavan, and R. W. Fessenden, Mellon Institute of Science, Radiation Research Laboratories, Quarterly Report RRL-3238-551 (Q-75), April 8, 1976.
(16) C. Moritz and R. Wolffenstein, *Chem. Ber.*, **32**, 432, 2531 (1899).
(17) R. G. R. Bacon and J. R. Doggart, *J. Chem. Soc.*, 1732 (1960).
(18) M. K. Eberhardt and M. Yoshida, *J. Phys. Chem.*, **77**, 589 (1973).
(19) R. Köster and K. D. Asmus, *J. Phys. Chem.*, **77**, 749 (1973).
(20) C. R. E. Jefcoate, J. R. Lindsay, and R. O. C. Norman, *J. Chem. Soc. B*, 1013 (1969).
(21) L. G. Shevchuck and N. A. Vysotskaya, *Zh. Org. Khim.* **4**, 1936 (1968).

Studies on Selective Preparation of Aromatic Compounds. 12. Selective Reductive Dehalogenation of Some Halophenols with Zinc Powder in Basic and Acidic Media[1]

Masashi Tashiro* and Gouki Fukata

Research Institute of Industrial Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

Received June 17, 1976

The reductive dehalogenation of 2,4,6-trihalophenols (**1a–c**), *m*-alkylhalophenols (**7a–c** and **8c**), and *o*-alkylhalophenols (**15a–e**) were carried out with zinc powder in basic and acidic media under various conditions. 2-Bromo-6-chloro- (**3a**), 2,4-dichloro- (**3b**), 2-chloro- (**4a**), 2,6-dichloro-3-methyl- (**10b**), 2-bromo-6-chloro-3-*tert*-butyl- (**10c**), 6-bromo-3-*tert*-butyl- (**11c**), 2-chloro-3-*tert*-butyl- (**12c**), 6-bromo-2-*tert*-butyl- (**17a**), and 6-chloro-2-*tert*-butylphenol (**17b**) were selectively prepared by reduction with zinc powder in basic medium such as 10% sodium hydroxide solution. The reductive dehalogenation of halophenols with zinc powder in acidic media such as 10% HCl aqueous–EtOH and Zn–AcOH was also discussed in this paper.

It has been previously reported that *tert*-butyl,[2-5] chloro,[6,7] and bromo groups[6-8] could serve as positional protective groups for the preparation of some phenolic compounds. In the previous paper,[1] 2-bromo- and 2,4-dibromophenol were prepared in good yields by the selective reductive debromination of 2,4,6-tribromophenol with zinc powder in 10% sodium hydroxide and 10% hydrochloric acid–ethanol solution, respectively.

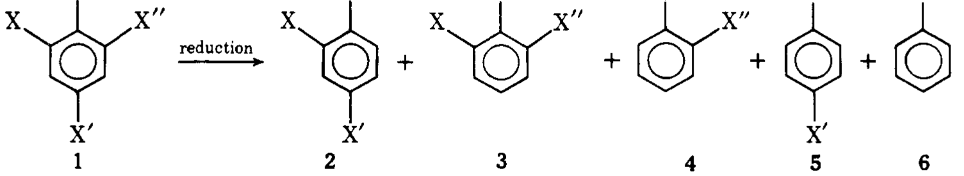
This paper presents additional applications of the selective reductive dehalogenation of halophenols with zinc powder in basic or acidic media.

Results and Discussion

The reductive dehalogenations of 2,4-dibromo-6-chlorophenol (**1a**), 4-bromo-2,6-dichloro- (**1b**), and 2,4,6-trichlorophenol (**1c**) were carried out under various conditions as summarized in Table I. Possible reductions products are **2**, **3**, **4**, **5**, and **6**.

Unlike 2,4,6-tribromophenol,[9] the treatment of **1a** with zinc

Scheme I



1 2 3 4 5 6

1

	X	X′	X″
a	Br	Br	Cl
b	Cl	Cl	Br
c	Cl	Cl	Cl

2

	X	X′
a	Br	Br
b	Br	Cl
c	Cl	Br
d	Cl	Cl

3

	X	X″
a	Br	Cl
b	Cl	Cl

4

	X″
a	Br
b	Cl

5

	X′
a	Br
b	Cl

Table I. Reductive Dehalogenation of Halophenols with Zinc Powder in Basic and Acidic Media

Run	Substrate	Method[a]	Temp, °C	Time, h	Product (%)
1	**1a**	A	Reflux	2	**1a** (100)
2	**1a**	B	Reflux	2	**1a** (100)
3	**1a**	C	20	2	**3a** (85)
4	**1a**	C	100	0.5	**4b** (86)
5	**1b**	C	100	1	**3b** (76)
6	**1c**	C	100	2	**1c** (100)
7	**1c**	D	20	2	**6** (100)
8[b]	**7a**	C	100	2	**8a** (0.5), **9a** (0.5), **10a** (5), **11a** (41), **12a** (37), **14a** (16)
9[b]	**7a**	C	20	2	**7a** (9), **8a** (9), **9a** (10), **10a** (63), **11a** (4), **12a** (5)
10	**7b**	C	100	1	**10b** (84)
11	**7c**	C	100	5	**12c** (96)
12	**7c**	C	20	0.5	**10c** (84)
13	**7c**	A	Reflux	1	**10c** (91)
14	**8c**	C	20	1	**11c** (83)
15	**15a**	C	20	0.5	**17a** (87)
16	**15b**	C	20	0.5	**17b** (83)
17[b]	**15c**	C	100	0.5	**17a** (67), **18** (33)
18	**15d**	C	100	1	**17b** (82)
19	**15e**	C	100	2	**15e** (100)

[a] A, Zn–10% HCl aqueous–EtOH; B, Zn–AcOH; C, Zn–10% NaOH aqueous; D, Ni–Al–10% NaOH aqueous. [b] The distribution of products was shown.

powder in acidic media afforded no reduction product; **1a** was quantitatively recovered. In contrast 10% NaOH solution selectively gave only 2-bromo-6-chlorophenol (**3a**) at 20 °C, and 2-chlorophenol (**4b**) at 80 °C.

Similarly 2,6-dichlorophenol (**3b**) was obtained in good yield from the reduction of **1b** in zinc–10% NaOH solution. However, the same treatment of **1c** gave no reduction although treatment with Raney Ni-Al alloy in 10% NaOH solution even at 20 °C gave phenol (**6**) in quantitative yield.

Thus the *p*-bromo group of **1a** was more easily debrominated than *o*-bromo while a chloro group was not removed with zinc powder in 10% NaOH solution.

This synthetic route to **3a, 3b,** and **4b** is useful as **3a** and **3b** cannot be prepared by the directive halogenation of **6**, and the separation of pure **4b** from the mixture of chlorination of **6** is not easy. The indirect method for the preparation of **3a, 3b,** and **4b** was previously reported.[2]

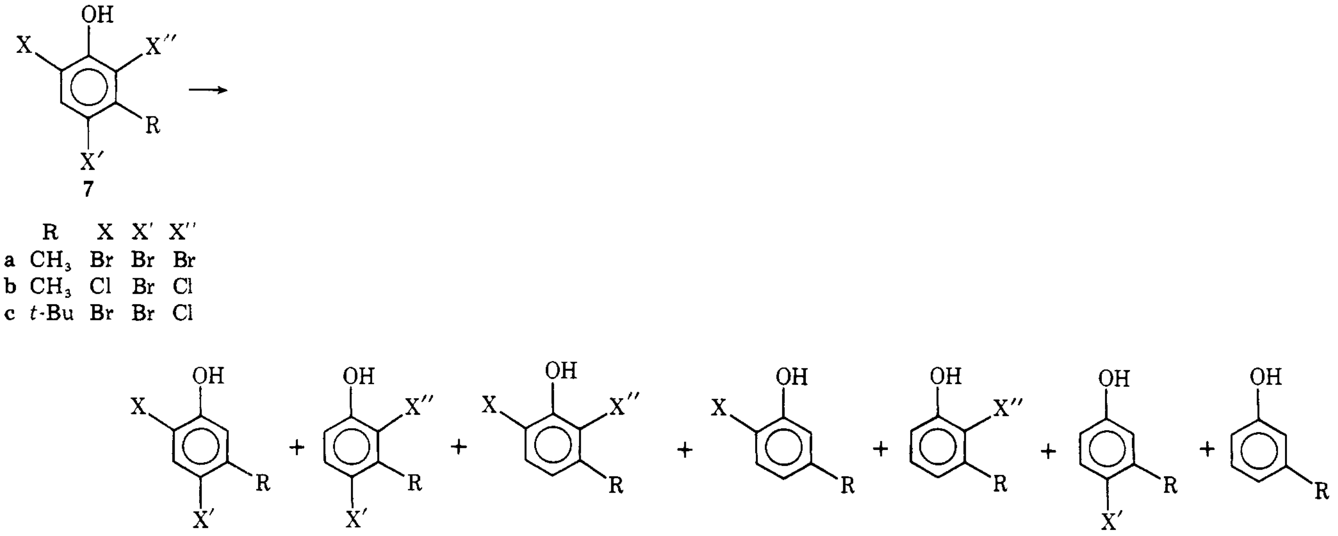
The compounds **4a** and **4b** were prepared by the $AlCl_3$–CH_3NO_2 catalyzed transalkylation of 4-*tert*-butyl-2-halophenol, and **3a** and **3b** were also obtained by $AlCl_3$–CH_3NO_2 catalyzed transalkylation of the corresponding 4-*tert*-butyl-2,6-dihalophenols.

However, the present method seem to be more handy than the previous work, since the starting compound in one-step preparation of **3a** and **4b** is same, that is, **1a.**

The reductive dehalogenations of the following *m*-alkylphenols, 2,4,6-tribromo-3-methyl- (**7a**), 4-bromo-2,6-dichloro-3-methyl- (**7b**), 4,6-dibromo-2-chloro-3-*tert*-butyl- (**7c**), and 4,6-dibromo-3-*tert*-butylphenol (**8c**), were carried out with zinc powder in basic and acidic media, and the results are summarized in Table I. Seven possible products are **8, 9, 10, 11, 12, 13,** and **14** (Scheme II).

Although the reaction of **7a** at 80 and 20 °C reaction temperature afforded many products as shown in runs 8 and 9, the

Scheme II



7

	R	X	X′	X″
a	CH_3	Br	Br	Br
b	CH_3	Cl	Br	Cl
c	*t*-Bu	Br	Br	Cl

8

	R	X	X′
a	CH_3	Br	Br
b	CH_3	Cl	Br
c	*t*-Bu	Br	Br

9

	R	X′	X″
a	CH_3	Br	Br
b	CH_3	Br	Cl
c	*t*-Bu	Br	Cl

10

	R	X	X″
a	CH_3	Br	Br
b	CH_3	Cl	Cl
c	*t*-Bu	Br	Cl

11

	R	X
a	CH_3	Br
b	CH_3	Cl
c	*t*-Bu	Br

12

	R	X″
a	CH_3	Br
b	CH_3	Cl
c	*t*-Bu	Cl

13

	R	X′
a	CH_3	Br
b	*t*-Bu	Br

14

	R
a	CH_3
b	*t*-Bu

main products at 80 °C are **11a** and **12a**; that at 20 °C is **10a**. Thus some selectivity in the reduction of **7a** was observed.

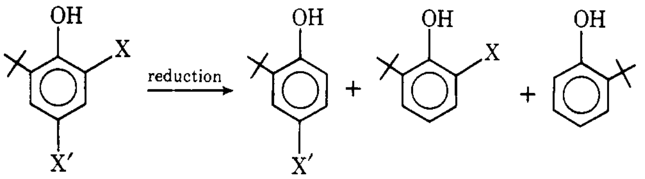
In contrast to the mixture from **7a**, **7b** afforded a high yield of 2,6-dichloro-*m*-cresol (**10b**) by the selective reduction of the *p*-bromo group. Highly selective reductive debromination was observed for **7c** and **8c** also as shown in runs 11, 12, and 14. That is, the desired product, 6-bromo-2-chloro-3-*tert*-butylphenol (**10c**), was obtained in good yield from the reduction of **7c** at 20 °C in basic media, and 2-chloro-3-*tert*-butylphenol (**12c**) was obtained in good yield at 80 °C reaction temperature. Also 6-bromo-3-*tert*-butylphenol (**11c**) was selectively formed in the reduction of **8c**.

Reductive debromination of **7c** in acidic medium resulted in loss of the *p*-bromo group to form **10c** rather than loss of *o*-bromo group to form **9c** which would be analogous to loss of *o*-bromo group by 2,4,6-tribromophenol in acidic media.[1,9]

The structures of **10b**, **10c**, **11c**, and **12c** were confirmed by their spectral data as well as elemental analyses. This selective reduction was applicable to **10b**, **10c**, **11c**, and **12c** as well as **3a**, **3b**, and **4b**, but not applicable to the reductive dehalogenation of **7a** owing to formation of a mixture.

Next examined was the possibility that the desired 2-*tert*-butylhalophenols could be prepared by the reductive dehalogenation of the corresponding 2-*tert*-butyldihalophenols (**15**). Reductions of 6-bromo-4-iodo- (**15a**), 6-chloro-4-iodo- (**15b**), 4,6-dibromo- (**15c**), 4-bromo-6-chloro- (**15d**), and 4,6-dichloro-2-*tert*-butylphenol (**15e**) were carried out with zinc powder in 10% NaOH solution as summarized in Table I.

Scheme III



15

	X	X'
a	Br	I
b	Cl	I
c	Br	Br
d	Cl	Br
e	Cl	Cl

16

	X'
a	I
b	Br
c	Cl

17

	X
a	Br
b	Cl

18

The expected products, 6-bromo- (**17a**) and 6-chloro-2-*tert*-butylphenol (**17b**), were obtained in good yields from **15a** and **15b** at 20 °C. However, the reduction of **15c** at 20 °C afforded 4-bromo-2-*tert*-butylphenol (**16b**) and **17a** with large amount of the recovered **15c**, while at 100 °C **17a** and 2-*tert*-butylphenol (**18**) were obtained. Also **17b** was selectively prepared in good yield by the reduction of **15a** at 100 °C. In the case of **15e**, no reduction product was obtained and starting compound **15e** was recovered in quantitative yield.

The structures of **17a** and **17b** were confirmed by their spectral data as well as elemental analyses. The bromination of **17a** and **17b** with molecular bromine in MeOH afforded **15c** and **15d**, which were also prepared by the bromination of **18** and **17b**, respectively. These results support the structure assigned to **17a** and **17b**.

Results indicate that the iodo group is more easily removed than the bromo group and that the chloro group is never removed under these conditions. Thus bromine and iodine can serve as positional protective groups for the preparations of chlorophenols, as they can be removed with zinc powder in 10% NaOH solution. It is also interesting that zinc powder in basic medium removes the *p*-bromo group more easily than the *o*-bromo group to afford *o*-bromophenols.

An unidentified dark-violet compound[10] was precipitated in good yield when a solution of **15a**, **15b**, and **15c** in 10% NaOH was kept at room temperature for a few minutes. Therefore, it should be noted that **15a**, **15b**, **15c**, and **15d** must be added to the suspension of zinc powder in 10% NaOH solution.

Experimental Section

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

Analytical Procedure. The analyses were carried out by gas chromatography using a Yanagimoto gas chromatograph, Yanaco YR-101: column, 30% high vacuum silicon grease, 75 cm; increase rate of column temperature, 12 °C/min, carrier gas hydrogen, 30 ml/min.

From the areas of individual peaks, mol % figures were calculated for each product after the relative response data had been determined by the internal standard method. Nitrobenzene was used as an internal standard substance.

Reduction of 2,4-Dibromo-6-chlorophenol (1a). A. Using Zn–10% HCl–EtOH. To a mixture of 0.5 g (1.85 mmol) of **1a**,[11] 0.5 g of zinc powder, and 15 ml of ethanol was added 2.5 ml of 10% hydrochloric acid. After the reaction mixture was refluxed for 1 h, unchanged zinc powder was removed by filtration. The filtrate was evaporated in vacuo leaving 0.5 g (100%) of **1a**.

B. Using Zn–AcOH. To a solution of 0.5 g of **1a** in 15 ml of acetic acid was added 0.5 g of zinc powder. After the reaction mixture was refluxed for 1 h, the unchanged zinc powder was removed by filtration. The filtrate was poured into a large amount of water and extracted with benzene. The benzene extract was washed with water, dried over sodium sulfate, and evaporated in vacuo to afford 0.5 g (100%) of **1a**.

C. In Zn–10% NaOH at 20 °C. To a solution of 2.0 g (7.4 mmol) of **1a** in 20 ml of 10% sodium hydroxide was added 4 g of zinc powder at 20 °C. After the reaction mixture was stirred at 20 °C for 2 h, the unchanged zinc powder was filtered off. The filtrate was acidified with 10% hydrochloric acid and extracted with benzene. The benzene extracted was dried over sodium sulfate and evaporated in vacuo, leaving 1.2 g (85%) of **3a** which has been prepared as previously reported.[2]

D. In Zn–10% NaOH at 100 °C. To a solution of 2 g of **1a** in 20 ml of 10% sodium hydroxide was added 4 g of zinc powder. The reaction mixture was heated at 100 °C under stirring for 30 min, then treated and worked up as described above to afford 0.71 g (86%) of **4b**.

Reduction of 4-Bromo-2,6-dichlorophenol (1b). To a solution of 2.0 g (8.27 mmol) of **1b**[12] in 20 ml of 10% sodium hydroxide was added 4 g of zinc powder. The reaction mixture was stirred at 100 °C for 1 h, then treated and worked up as described above, affording 1.03 g (76%) of **3b** which was prepared as previously reported.[2,8,13]

Reduction of 2,4,6-Trichlorophenol (1c). A. In Zn–10% NaOH. After a mixture of 2 g (10.13 mmol) of **1c**, 4 g of zinc powder, and 20 ml of 10% sodium hydroxide was heated at 100 °C for 2 h, the reaction mixture was treated and worked up as described above, affording 2 g of **1c**.

B. In Raney Alloy–10% NaOH. To a solution of 0.1 g (0.51 mmol) of **1c** in 3 ml of 10% sodium hydroxide was added 0.2 g of Raney Ni-Al alloy at 20 °C under stirring and the stirring was continued for 2 h. The reaction mixture was treated and worked up as described above, affording **6** in quantitative yield.

Reduction of 2,4,6-Tribromo-*m*-cresol (7a). To a solution of 2 g (5.8 mmol) of **7a**[14] in 20 ml of 10% sodium hydroxide was added 4 g of zinc powder. The reaction mixture was stirred at 20 and 100 °C for 2 h, respectively, and then both reaction mixture were treated and worked up, affording 1.37 and 0.75 g of oily products which were analyzed by gas chromatography. The results are shown in Table I. The structure of these products were determined by comparison with authentic samples. The authentic samples of **8a**,[15] **9a**,[2] **11a**,[16] and **12a**[17] were prepared according to the reported method.

Reduction of 4-Bromo-2,6-dichloro-*m*-cresol (7b). To a solution of 2 g (7.24 mmol) of **7b**[12] in 20 ml of 10% sodium hydroxide was added 4 g of zinc powder. The reaction mixture was stirred at 100 °C for 1 h, and then worked up as described above, affording 1.2 g (84%) of **10b** which was identified with an authentic sample,[8] mp 26–28 °C.

Reduction of 4,6-Dibromo-2-chloro-3-*tert*-butylphenol (7c).[18] **A. At 100 °C.** To a solution of 2 g (5.84 mmol) of **7c** in 20 ml of 10% sodium hydroxide was added 4 g of zinc powder. The reaction mixture was stirred at 100 °C for 5 h, and then treated and worked up as described above, affording 0.75 g (70%) of **12c** as a colorless oil: bp 233 °C (760 mm); IR (NaCl plate) 3540 cm^{-1} (ν_{OH}); NMR (CCl_4) δ 1.45 [9 H, s, $(CH_3)_3$], 5.75 (1 H, broad s, OH), 6.7–7.00 (3 H, m, aromatic protons). Anal. Calcd for $C_{10}H_{13}OCl$: C, 65.04; H, 7.09. Found: C, 64.66; H, 6.35.

B. At 20 °C. To a solution of 1 g (2.92 mmol) of **7c** in 15 ml of 10% sodium hydroxide was added 2 g of zinc powder. The reaction mixture was stirred at 20 °C for 30 min and then treated and worked up as described above, affording 0.65 g (84%) of **10c** as colorless prisms (*n*-hexane): IR (KBr) 3420 cm^{-1} (ν_{OH}); NMR (CCl_4) δ 1.45 [9 H, s, $CH_3)_3$], 5.95 (1 H, broad s, OH), 6.78 and 7.26 (each 1 H, s, J = 8.25 Hz, aromatic protons). Anal. Calcd for $C_{10}H_{12}OClBr$: C, 45.57; H, 4.59. Found: C, 45.32; H, 4.76.

C. In Acidic Medium. A mixture of 2 g of **7c,** 60 ml of ethanol, 10 ml of 10% hydrochloric acid, and 2 g of zinc powder was refluxed and then treated and worked up as described above, affording 1.4 g (91%) of **10c.**

Reduction of 4,6-Dibromo-3-*tert*-butylphenol (8c). To a suspension of 3 g (9.74 mmol) of **8c**[18] in 30 ml of 10% sodium hydroxide was added 6 g of zinc powder. After the reaction mixture was stirred at 20 °C for 2 h, it was treated and worked up as described, affording 1.85 g (83%) of **11c.**[18]

2-*tert*-Butyl-4-iodophenol (16a). To a solution of 45 g (300 mmol) of **15a** was added 50 g (308 mmol) of ICl in 40 ml of acetic acid at 25 °C under stirring, and the reaction mixture was stirred for 3 h, longer, then it was poured into a large amount of water and extracted with benzene. The benzene extract was washed with aqueous $Na_2S_2O_3$ solution, dried over Na_2SO_4, and evaporated in vacuo to leave 60 g of crude 1 which was purified by distillation under reduced pressure to afford 50 g (60.4%) of **16a:** bp 106–108 °C (3 mm); IR (KBr) 3560 cm^{-1} (ν_{OH}); ^1H NMR (CCl_4) δ 1.36 (s, 9, *t*-CH_3), 4.60 (s, 1, OH), 6.30 (d, J_{ac} = 8.25 Hz), 7.24 (dd, J_{ac} = 8.25, J_{ab} = 3.0 Hz), and 7.24 (s, J_{ab} = 3.0 Hz, each 1, aromatic protons). Anal. Calcd for $C_{10}H_{13}OI$: C, 43.50; H, 4.75. Found: C, 43.17; H, 4.64.

2-Chloro-4-iodo-6-*tert*-butylphenol (15b). To a solution of 5.53 g (20 mmol) of **16a** in 15 ml of CH_3NO_2 was gradually added 5 g (37 mmol) of SO_2Cl_2 at 20 °C. After the reaction mixture was kept at 20 °C for 10 min, it was poured into a large amount of water and extracted with benzene. The benzene extract was dried over Na_2SO_4 and evaporated in vacuo to leave pale yellow, resinous material which was treated with a small amount of MeOH–H_2O to afford 3.80 g (61.2%) of **15b,** mp 45.5–47.0 °C, colorless prisms recrystallized from a mixed solvent, MeOH–H_2O (1:1): IR (KBr) 3540, 3500 cm^{-1} (ν_{OH}); ^1H NMR ($CDCl_3$) δ 1.37 [s, 9, $(CH_3)_3$], 5.85 (s, 1, OH), 7.42 and 7.51 (d, J_{ab} = 2.25 Hz, each 1, aromatic protons). Anal. Calcd for $C_{10}H_{12}OClI$: C, 38.67; H, 3.90. Found: C, 38.98; H, 3.80.

2-Bromo-4-iodo-6-*tert*-butylphenol (15a). To a solution of 14 g (51 mmol) of **16a** in 50 ml of MeOH was added gradually 9 g (56 mmol) of Br_2 at 5–10 °C. After the reaction mixture was kept at 25 °C for 30 min, it was poured into a large amount of water to give 17 g (94.4%) of **15a,** mp 67–67.5 °C, as colorless needles recrystallized from MeOH–H_2O: IR (KBr) 3520, 3500 cm^{-1} (ν_{OH}); ^1H NMR (CCl_4) δ 1.38 [s, 9, $C(CH_3)_3$], 5.73 (s, 1, OH), 7.39 and 7.59 (d, J_{ab} = 2.25 Hz, each 1, aromatic protons). Anal. Calcd for $C_{10}H_{12}OBrI$: C, 33.83; H, 3.41. Found: C, 34.06; H, 3.36.

2-Chloro-6-*tert*-butylphenol (17b). To a suspension of 5 g of zinc powder in 30 ml of 10% NaOH was added 3.1 g (10 mmol) of **15b** at 28 °C in the period of 15 min under stirring, and the stirring was continued for 15 min longer. After the reaction mixture was warmed at 90 °C for 1 min, the unchanged Zn was filtered off. The filtrate was extracted with benzene. The benzene extract was dried over Na_2SO_4 and evaporated in vacuo, leaving 1.52 g (82.5%) of **17b,** bp 72–73 °C (3 mm), as a pale yellow liquid: IR (KBr) 3560 cm^{-1} (ν_{OH}); ^1H NMR (CCl_4) δ 1.38 (s, 9, *t*-CH_3), 5.76 (s, 1, OH), 6.55–7.20 (m, 3, aromatic protons). Anal. Calcd for $C_{10}H_{13}OCl$: C, 65.04; H, 7.10. Found: C, 64.83; H, 7.06.

2-Bromo-6-*tert*-butylphenol (17a). To a suspension of 15 g of zinc powder in 100 ml of 10% NaOH was added 10 g (28 mmol) of **15a** and the reaction mixture was treated and worked up as described above, affording 5.58 g (86.5%) of **17a,** bp 80–81 °C (3 mm), as a pale yellow liquid: IR (KBr) 3530 cm^{-1} (ν_{OH}); ^1H NMR (CCl_3) δ 1.38 (s, 9, *t*-CH_3), 5.72 (s, 1, OH), and 6.64–7.26 (m, 3, aromatic protons). Anal. Calcd for $C_{10}H_{13}OBr$: C, 52.42; H, 5.72. Found: C, 51.90; H, 5.62.

2,4-Dibromo-6-*tert*-butylphenol (15c). A. Bromination of 18. To a solution of 25 g (166.4 mmol) of **18** in 50 ml of MeOH was added 55 g (343.8 mmol) of Br_2 at room temperature. The reaction mixture was stirred for 10 min and evaporated in vacuo, affording 51.2 g (99.9%) of **15c,** mp 57–58 °C, as colorless prisms (MeOH–H_2O).

B. Bromination of 17a. To a solution of 100 mg (0.44 mmol) of **17a** in 2 ml of MeOH was added 0.2 g (1.35 mmol) of Br_2, and the reaction mixture was treated and worked up as described above, affording 130 mg (96.7%) of **15c,** mp 57–58 °C.

Reduction of 4,6-Dibromo-2-*tert*-butylphenol (15c). To a suspension of 10 g of zinc powder in 50 ml of 10% sodium hydroxide was added 0.16 g (20 ml) of **15c.**[19] After the reaction mixture was stirred at 100 °C for 30 min, it was treated and worked up as described above, affording 3.0 g of oily material which was analyzed by gas chromatography, and the result is shown in Table I.

4-Bromo-6-chloro-2-*tert*-butylphenol (15d). To a solution of 11.5 g (50 mmol) of 2-*tert*-butylphenol[20] in 50 ml of nitromethane was added 10 g (75 mmol) of sulfuryl chloride at 25 °C. After the reaction mixture was stirred for 30 min, it was poured into a large amount of ice–water and extracted with benzene. The benzene extract was dried over sodium sulfate and evaporated in vacuo, leaving 10 g of crude material which was chromatographed over silica gel using benzene as an eluent, affording 8.5 g (64.5%) of **15d** as pale yellow product: mp 39.5–41.0 °C; IR (KBr) 3520 cm^{-1} (ν_{OH}); NMR (CCl_3) δ 1.39 [9 H, s, $(CH_3)_3$], 5.75 (1 H, s, OH), 7.22 and 7.32 (each 1 H, d, J = 2.25 Hz, aromatic protons). Anal. Calcd for $C_{10}H_{12}OBrCl$: C, 45.57; H, 4.59. Found: C, 45.48; H, 4.48.

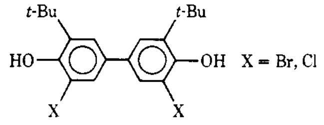
Bromination of 17b. To a solution of 0.19 g (1 mmol) of **17b** was added gradually a solution of 0.2 g (1.25 mmol) of bromine in 2 ml of CCl_4 at 20 °C. The reaction mixture was stirred for 2 h and evaporated in vacuo to leave 0.25 g of oily product which was chromatographed over silica gel using benzene as an eluent, affording 0.19 g (70%) of **15d.**

Reduction of 4-Bromo-6-chloro-2-*tert*-butylphenol (15d). To a suspension of 2 g of zinc powder in 15 ml of 10% sodium hydroxide was added 1 g (3.8 mmol) of **15d.** After the reaction mixture was stirred at 100 °C for 1 h, it was treated and worked up as described above, affording 0.56 g (80%) of **17b.**

Registry No.—**1a,** 4526-56-1; **1b,** 3219-15-0; **1c,** 88-06-2; **7a,** 4619-74-3; **7b,** 56037-74-2; **7c,** 60935-47-9; **8c,** 1131-12-0; **10b,** 13481-70-4; **10c,** 60935-48-0; **12c,** 60935-49-1; **15a,** 60803-27-2; **15b,** 60803-28-3; **15c,** 15460-12-5; **15d,** 60935-50-4; **15e,** 13395-86-3; **16a,** 60803-25-0; **17a,** 23159-87-7; **17b,** 4237-37-0; **18,** 88-18-6; zinc, 7440-66-6.

References and Notes

(1) Part 11: M. Tashiro and G. Fukata, *Org. Prep. Proced. Int.*, in press.
(2) M. Tashiro, H. Watanabe, and O. Tsuge, *Org. Prep. Proced. Int.*, **6,** 107 (1974).
(3) M. Tashiro, H. Watanabe, and O. Tsuge, *Org. Prep. Proced. Int.*, **6,** 117 (1974).
(4) M. Tashiro, G. Fukata, S. Mataka, and K. Oe, *Org. Prep. Proced. Int.*, **7,** 225 (1975).
(5) M. Tashiro, H. Watanabe, K. Oe, and O. Tsuge, *Org. Prep. Proced. Int.*, **7,** 255 (1975).
(6) M. Tashiro, G. Fukata, and K. Oe, *Org. Prep. Proced. Int.*, **7,** 237 (1975).
(7) M. Tashiro, G. Fukata, and K. Oe, *Org. Prep. Proced. Int.*, **7,** 183 (1975).
(8) M. Tashiro, H. Watanabe, and O. Tsuge, *Org. Prep. Proced. Int.*, **7,** 43 (1975).
(9) M. Kohn and J. Pteifer, *Monatsh. Chem.*, **48,** 211 (1927).
(10) When the dark violet compounds from **15a, 15b,** and **15c** were treated with zinc powder in AcOH, the corresponding biphenyl derivatives were obtained in good yields.



(11) M. Kohn and F. Rabinowitsch, *Monatsh. Chem.*, **48,** 347 (1927).
(12) R. Adams and C. S. Marvel, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1941, p 128.
(13) M. Tashiro, H. Watanabe, and K. Oe, *Org. Prep. Proced. Int.*, **7,** 189 (1975).
(14) M. Kohn and A. Segel, *Monatsh. Chem.*, **46,** 661 (1925).
(15) I. R. Gibbs and P. W. Robertson, *J. Chem. Soc.*, **105,** 1888 (1914).
(16) H. H. Hodgson and F. H. Moore, *J. Chem. Soc.*, 2038 (1926).
(17) H. H. Hodgson and H. G. Bread, *J. Chem. Soc.*, 127, 498 (1925).
(18) W. W. Haeding, *J. Org. Chem.*, **26,** 4851 (1961).
(19) M. Tsubota, *Nippon Kagaku Zasshi*, **89,** 602 (1968).
(20) A. J. Kolka, J. P. Napolitano, A. H. Filbey, and G. G. Ecke, *J. Org. Chem.*, **22,** 642 (1957).