# Oxidation of Arylmagnesium Bromides or Aryllithium to Phenols

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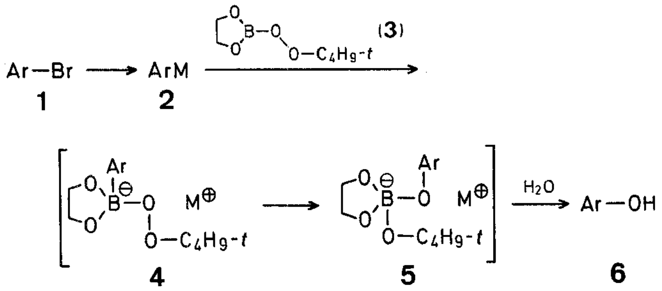
We report here a novel generation of ate complexes of the type **4** from arylmetal compounds (**2**) and the peroxyborate **3**. Since related ate complexes, formed in a different way, have been shown to rearrange to complexes **5**[1], the reaction of arylmagnesium halides or aryllithium (**2**) with **3** to **4** provides a convenient method for the conversion of aryl halides (**1**) into phenols (**6**).



M = Li, MgBr

On a laboratory scale, the conversion **1**→**2**→**6** has hitherto been achieved[2] mainly by two different procedures:

- Method A: Oxidation of the arylmetal derivative **2** with the magnesium salt of *t*-butyl hydroperoxide (thus for example, phenol is obtained from phenylmagnesium bromide in 80% yield[3]);
- Method B: Reaction of the arylmetal derivative **2** with trimethyl borate to give a boronic acid derivative which is *in situ* oxidized with hydrogen peroxide[4] (a related, more expensive modification uses borane instead of trimethyl borate[5]).

Our new procedure (Method C) is related to both of the above-mentioned procedures. It uses 2-*t*-butylperoxy-1,3,2-dioxaborolane (**3**) as oxidizing agent. Reagent **3** is prepared

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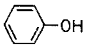
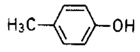
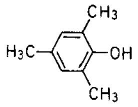
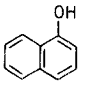
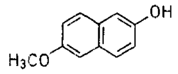
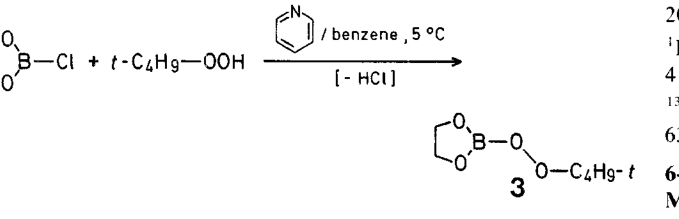
**Table.** Phenols (**6**) prepared from Aryl Bromides (**1**) via the Arylmagnesium Bromides (**2**, M=MgBr) or the Aryllithium Compounds (**2** M=Li) using 2-*t*-Butylperoxy-1,3,2-dioxaborolane (**3**) as Oxidizing Agent (Method C)

| Product **6** | Yield [%] by Method |  |  |  |  |  | m.p. [°C] |  |
|---|---|---|---|---|---|---|---|---|
|  | A |  | B |  | C[a] |  | found | reported |
|  | Ar—MgBr | ArLi | Ar—MgBr | ArLi | Ar—MgBr | ArLi |  |  |
| **a**  | 80[3] | 47[3] |  | 72-86[5] | 79[b] | 66[b] | [95-96°][b] | [95-96°][b,7] |
| **b**  |  |  |  | 53[5] | 91 | 83 | 32-33°; 34° | 34.8°[7] |
| **c**  |  |  |  |  | 14 |  | 69-71° | 72°[7] |
| **d**  |  |  |  |  | 94 | 63 | 94° | 96°[7] |
| **e**  |  |  | 73-81[4] |  | 91 |  | 148° | 148-149°[4] |

[a] The new method described in this communication.

[b] Isolated as 2,4,6-tribromophenol.

from 2-chloro-1,3,2-dioxaborolane[6] and *t*-butyl hydroperoxide in benzene in the presence of pyridine.



A freshly prepared solution of the aryllithium compound **2** (M=Li) or the arylmagnesium bromide **2** (M=MgBr) in tetrahydrofuran is added to a solution of the crude reagent **3** in tetrahydrofuran. Work-up after an appropriate reaction time affords the corresponding phenol **6** in high yield (up to 94%) except for sterically hindered phenols such as 2,4,6-trimethylphenol. In this latter case, the low yield (14%) is probably due to only partial formation of the ate complex **4** as witnessed by the high yield of mesitylene (74%) formed upon hydrolysis.

The reaction has been extended to the conversion of octylmagnesium bromide and octyllithium into octanol (80 and 74% yield, respectively). However, less basic organometallic compounds, such as enolates, cyclopentadienide, or acetylenides could not similarly be oxidized. Hence, the new method may find application mainly in the conversion of arylmetal compounds to phenols. As long as the reagent **3** is not yet commercially available, the inconvenience of its preparation may well be balanced by the cleanliness of the reaction **2**→**6**.

### 2-*t*-Butylperoxy-1,3,2-dioxaborolane (3):

A 2.93 molar solution (6.85 ml, 20.1 mmol) of *t*-butyl hydroperoxide in benzene is mixed with dry pyridine (1.58 g, 20.0 mmol). This mixture is added to a stirred solution of 2-chloro-1,3,2-dioxaborolane[6] (2.12 g, 20.0 mmol) in benzene (25 ml) at 5 °C. The precipitation of pyridine hydrochloride is completed by the addition of ether (20 ml). Stirring is continued for 2 h and the pyridine hydrochloride then filtered off. The filtrate is concentrated in vacuo and the residue dried at 0.001 torr for 2 h to give crude **3** as a viscous oil; yield: 3.35 g. The product contains 6.5% benzene according to N.M.R. analysis. Also according to N.M.R. analysis, the crude product **3** thus prepared is a mixture of monomeric **3** and higher aggregates.

Active Oxygen Content (iodometric titration): 19.89% (calculated: 20.00%).

$^{1}$H-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 1.24-1.33$ (m, 9H); 4.0-4.3 ppm (m, 4H).

$^{13}$C-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 23.86$, 24.41, 24.56, 25.57, 63.28, 63.38, 63.47, 64.28, 64.76, 65.60, 81.14, 81.45, 81.56, 82.00 ppm.

### 6-Methoxy-2-naphthol (6e) from 2-Bromo-6-methoxynaphthalene by Method C; Typical Procedure:

A solution of 6-methoxy-2-naphthylmagnesium bromide (20.0 mmol) is prepared[4] from 2-bromo-6-methoxynaphthalene (4.97 g, 20.0 mmol) and flame-dried magnesium (0.534 g, 22 mmol) in tetrahydrofuran (25 ml) and this solution is slowly added to a stirred solution of 2-*t*-butylperoxy-1,3,2-dioxaborolane (**3**; 3.20 g, 20.0 mmol) in tetrahydrofuran (20 ml). [The ate complex **4** may in some cases precipitate as a gummy material.] The mixture is allowed to stand overnight, then refluxed for 3 h, and hydrolyzed by the addition of 2 normal hydrochloric acid (50 ml) at 0 °C with stirring. The organic phase is separated and the aqueous phase extracted with ether (2 × 50 ml). The combined organic phases are washed with water (6 × 100 ml) and dried with sodium sulfate. The solvent is removed in vacuo using a rotary evaporator and the residual product is crystallized from benzene/petroleum ether (1/3); yield of **6e**: 3.16 g (91%; 2.47 g first fraction + 0.69 g second fraction); m.p. 148 °C (Ref.[4], m.p. 148-149 °C).

$^{1}$H-N.M.R. ($DMSO-d_6/TMS_{int}$): $\delta = 3.85$ (s, 3H); 7.0-8.0 (m, 6H); 9.50 ppm (s, 1H).

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