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# **ORGANIC PEROXIDES**

### V. OXIDATION OF ARYLLITHIUM COMPOUNDS TO PHENOLS

### H. S. CHANG AND J. T. EDWARD

Low yields of phenols are obtained by the oxidation of arylmagnesium halides with molecular oxygen, but they may be improved by carrying out the oxidation in the presence of an aliphatic Grignard reagent (1). The reasons for this improvement have been discussed by Walling and Buckler (2). Aryllithium compounds are also oxidized to phenols by molecular oxygen in low yields (3, 4), and we have carried out the oxidation in the presence of butyllithium in the hope of improving the yield. This hope proved illusory, as shown by the results in Table I. Better yields were obtained when oxidation was effected by t-butyl hydroperoxide (cf. ref. 4), but were still sometimes low. The oxidations of the  $\alpha$ -furyllithium compounds were suggested by the successful oxidation of  $\alpha$ -thienyllithium (5), and expected to yield the unsaturated lactones tautomeric with the  $\alpha$ furanols (6); in the event, only intractable, high-boiling tars were obtained.

Yields (%) of phenols from the oxidation of aryllithium compounds with different oxidizing agents

|  | Oxidizing agent                    |                |                      |
|--|------------------------------------|----------------|----------------------|
| Compound   | $O_2^*$                            | $O_2 + BuLi^*$ | Bu <sup>t</sup> OOH† |
| Phenyllithium<br>p-Biphenylyllithium<br>2-Methoxy-1-naphthyllithium<br>α-Furyllithium<br>5-Methyl-2-furyllithium | $30 \ddagger 18 \parallel 7 0 0 0$ | 30<br>19<br>   | 93§<br>              |

\*Yield based on aryllithium compound. †Yield based on peroxide. ‡Gilman and Pacevitz (3) reported 22–25% yield. \$Müller and Töpel (4), using α-tetralyl hydroperoxide, reported 96% yield. Müller and Töpel (4) reported 3% yield.

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#### EXPERIMENTAL

#### Oxidation with Molecular Oxygen

The preparations of phenyllithium (7), p-biphenylyllithium (7),  $\alpha$ -furyllithium (8), and 5-methyl-2furyllithium (8) were carried out according to the literature; 2-methoxy-1-naphthyllithium was prepared in 80% yield (estimated by titration) from 1-bromo-2-methoxy naphthalene by the conventional procedure (7). Dry oxygen was bubbled through the ether solutions of the organolithium compounds for several hours. This represents a large excess of oxygen over that stoichiometrically required; in separate experiments it was shown that use of the stoichiometric quantity offered no advantage. The ether solutions were then worked up in the usual way.

Phenol, extracted from the ether solution with aqueous sodium hydroxide, was estimated in the extract by titration (9); this accounts for yields slightly higher than those reported (3, 4), which were based on the isolation of the product. p-Hydroxybiphenyl was isolated as a crystalline solid, m.p.161°, identified by mixed m.p. The phenolic fraction from the oxidation of 2-methoxy-1-naphthyllithium (0.014 mole) was obtained as a brown gum (0.58 g), which was chromatographed on Woelm alumina (activity II-III) in hexane solution. Elution with hexane-benzene 4:1 (v/v) gave 2-methoxy-1-naphthol as a gummy solid, crystallizing from hexane as colorless needles (0.17 g; 7%), m.p. 53.5-54.5°. Calc. for C<sub>11</sub>H<sub>10</sub>O<sub>2</sub>: C, 75.86; H, 5.75%. Found: C, 75.70; H, 5.78%. Infrared spectrum:  $\nu_{\text{max}}^{\text{CC14}}$  in cm<sup>-1</sup>: 3530 (m), 3040 (m), 2940 (m), 2820 (m). 1650 (m), 1600 (m), 1490 (s), 1410 (m), 1380 (m), 1360 (s), 1280 (s), 1200 (m), 1180 (w), 1100 (s), 1060 (s), 905 (s). Treatment of this compound with benzoyl chloride in pyridine gave an oily product. The oil in benzene solution was washed with aqueous alkali, dried over magnesium sulphate, and recovered by evaporation. It was then taken up in hexane and chromatographed on Woelm alumina (activity II-III). Elution with hexane-benzene 4:1 (v/v) gave 2-methoxy-1-naphthyl benzoate, crystallizing from hexane in colorless rods, m.p. 104-105°. Calc. for C18H14O3: C, 77.69; H, 5.03%. Found: C, 77.48; H, 4.93%. Infrared spectrum: p<sub>max</sub><sup>CCL</sup> in cm<sup>-1</sup>: 3050 (w), 3020 (w), 2985 (w), 2860 (w), 1750 (s), 1645 (m), 1609 (m), 1515 (w), 1485 (w), 1459 (m), 1385 (m), 1353 (w), 1318 (w), 1280 (s), 1247 (s), 1190 (m), 1175 (s), 1155 (m), 1150 (m), 1100 (s), 1080 (s), 1067 (s), 1023 (s), 923 (w), 695 (m). Chakravarti and Pasupati (10), who oxidized 2methoxy-1-naphthylmagnesium bromide with molecular oxygen, did not isolate the napthol, but converted it to 2-methoxy-1-naphthyl benzoate, m.p. 110°, in low, unspecified overall yield.

## Oxidation with t-Butyl Hydroperoxide

Commercial hydroperoxide (84% by titration; 1 mole) in anhydrous ether was added slowly to a stirred ether solution of the aryllithium compound (2.2 moles). Stirring was continued for 2-3 hours, and the mixture then poured into ice water and worked up in the usual fashion, Crystallization from hexane of the gummy phenolic fraction obtained from 2-methoxy-1-naphthyllithium gave white crystals (7% yield) decomposing above 288°, presumably of 4,4'-dihydroxy-3,8'-dimethoxy-1,1'-binaphthyl (cf. ref. 11), although a satisfactory analysis could not be obtained for the compound. Calc. for C22H18O4: C, 76.30; H, 5.20%. Found: C, 75.39; H, 5.02%. (Chakravarti and Pasupati (10) reported obtaining in unspecified yield from the oxidation of 2-methoxy-1-naphthylmagnesium bromide with molecular oxygen a solid melting above 300°, which they did not analyze.) However, the dibenzoate, obtained by treatment of the binaphthol with benzoyl chloride in pyridine, crystallized from benzene in colorless rods, m.p. 346-348°, of satisfactory purity. Calc. for C36H25O6: C, 77.97; H, 4.67%. Found: C, 77.98; H, 4.88%. The mother liquors from 4,4'dihydroxy-3,3'dimethoxy-1,1'-binaphthyl were chromatographed as before to yield 2-methoxy-1-naphthol (Table I).

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