prepared 1 (60.0 g) was added at such a rate that the temperature did not exceed −45 °C. After 3 h at −55 to −45 °C the mixture was allowed to come to room temperature during 3 h and was then poured on 2 L of cracked ice. As soon as the ice was melted the solid was collected and washed with cold water. After drying by suction overnight the distilled solid, bp 125 °C (0.4 mm), was recrystallized from benzene–petroleum ether to yield 33.0 g (61%) of colorless **2**, mp 115–116 °C.

Registry No.—**1**, 941-63-9; **2**, 4792-30-7; **3**, 37102-74-2; 5-acetyl-2-methylfuran, 1193-79-9; maleic anhydride, 108-31-6; 2-methylfuran, 534-22-5.

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(13) In our hands the melting point of **1** varies with the rate of heating, undoubtedly because of the ready reversibility of the DA reaction.[9]
(14) Sulfolane, tetramethylenesulfone, was kindly provided by the Phillips Petroleum Co., Bartlesville, Okla.

A Direct Method for the Preparation of Phenols from Aryl Bromides Utilizing Molybdenum Peroxide–Pyridine–Hexamethylphosphoramide

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We wish to report a convenient synthetic method for the conversion of aryl bromides to phenols by reactions of arylmagnesium bromide Grignard reagents with molybdenum peroxide–pyridine–hexamethylphosphoramide. The reported procedure represents a novel synthetic use of the molybdenum complex and provides a mild, one-flask reaction sequence for the synthesis of phenols under basic conditions. We obtained good to excellent yields with several prototype compounds.

Vedejs[1] had reported a method for the hydroxylation of enolate anions using transition metal peroxide MoO_5–Py–HMPA (MoOPH) as the hydroxylating agent. This MoOPH had been previously described by Mimoun for the epoxidation of olefins.[2,3] Regen and Whitesides[4] noted that a related reagent, MoO_5–HMPA, reacted with *n*-butyllithium to form *n*-butoxide and Vedejs[1] observed that a number of enolate anions reacted with this reagent at low temperature presumably by nucleophilic attack at peroxide oxygen. A variety of esters, lactones, and ketones having enolizable methine or methylene groups have been hydroxylated with this complex. Synthetic pathways under investigation in our laboratories made it desirable to study the effectiveness of MoOPH in converting aryl bromides to their respective phenolate anions. Aqueous workup with careful acidification yielded the phenolic products. We can now describe our application of MoOPH for the preparation of phenolic compounds.

Starting with an appropriate aromatic bromide we formed the arylmagnesium bromide in anhydrous THF and immediately reacted the Grignard reagent with MoOPH[5,6] at dry ice–acetone bath temperatures. After aqueous workup, the phenolic compounds were isolated in high yields (Table I). The method described is a straightforward and convenient one. Reactions run at temperature to 20 °C gave similar results but caution is advised when utilizing the MoOPH complex at room temperature.[7] Reactions of bromobenzene (**1**), 1-bromo-4-methoxybenzene (**2**), 1-bromo-4-ethylbenzene (**3**), and 1-bromonaphthalene (**4**) with MoOPH afforded the corresponding phenolic compounds in yields of 67–89%.[9]

Table I

Starting material[a]	Product[8]	Yield, %
Bromobenzene (**1**)	Phenol (**1a**)	89
1-Bromo-4-methoxybenzene (**2**)	4-Methoxyphenol (**2a**)	67
1-Bromo-4-ethylbenzene (**3**)	4-Ethylphenol (**3a**)	70
1-Bromonaphthalene (**4**)	1-Hydroxynaphthalene (**4a**)	85

[a] Compounds **1** and **4** were purifed by distillation. Compounds **2** and **3** were purified by column chromatography on silica gel (50:1, $CHCl_3$).

Experimental Section

All melting points were taken on a Thomas-Hoover melting point apparatus. IR spectra were obtained on a Beckman Model 4230 infrared spectrophotometer; NMR data were recorded on a Varian Model A-60A spectrometer in $CDCl_3$ using Me_4Si as an internal standard. TLC analysis was performed on silica gel plates using $CHCl_3$ as the mobile phase.

General Procedure for Making Arylmagnesium Bromides. Dry THF (15 mL) and 0.12 g (5.0 mmol) of Mg metal were placed in a three-necked flask equipped with a gas inlet tube, a gas outlet tube, and a dropping funnel. The aryl bromide (5.0 mmol) in 10 mL of dry THF was added dropwise with stirring under N_2 to the Mg–THF suspension. The reaction was allowed to proceed at room temperature and complete dissolution of Mg was taken as an indication of complete Grignard formation.

Reaction of the Grignard Reagent with MoOPH. After the formation of Grignard reagent, the dropping funnel was replaced with a ground glass stopper. The contents of the flask were cooled to −78 °C (dry ice–acetone bath). To this solution was added 5.0 mmol of powdered MoOPH.[2] The reaction was allowed to continue at −78 °C for 1 h at which time the flask was gradually warmed to 10 °C and 75 mL of H_2O was added. The reaction mixture was allowed to stir for an additional 1.0 h. The contents of the flask were extracted with $CHCl_3$ (3 × 100 mL), and the extracts washed with 10% HCl (1 × 30 mL) and 10% $NaHCO_3$ (1 × 30 mL). The solvent was removed under reduced pressure at 35 °C and the residue treated with 10% aqueous NaOH (25 mL). The alkaline solution was washed with $CHCl_3$ (2 × 50 mL), neutralized with 10% HCl to pH 4, and extracted with $CHCl_3$ (3 × 100 mL). The $CHCl_3$ layer was dried (Na_2SO_4) and evaporated to give the arylhydroxy compounds. The low-melting solids were purified by column chromatography (50:1 silica gel, $CHCl_3$) or by distillation. IR, NMR, and melting point data of all phenolic products were compared with those of authentic samples.

Registry No.—**1**, 108-86-1; **1a**, 108-95-2; **2**, 104-92-7; **2a**, 150-76-5; **3**, 1585-07-5; **3a**, 123-07-9; **4**, 90-11-9; **4a**, 90-15-3; MoOPH, 23319-63-3.

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(5) MoOPH was prepared according to the procedure of Mimoun (ref 2). We noted that while preparing the complex MoO_5–H_2O–HMPA allowing the temperature to rise above 40 °C results in a strongly exothermic reaction which is difficult to control.
(6) The reaction of phenylmagnesium bromide and MoOPH was studied between −78 and 20 °C. The reaction proceeded smoothly at 20 °C without any

explosion and without change in phenolic yields.
(7) Vedejs (ref 1) reported that MoO_5–H_2O–HMPA may be unstable when stored at room temperature. We stored this complex for 2 weeks and there was no indication of any instability. However, if the complex was exposed to air for 2–3 days it absorbed moisture and was exceedingly difficult to recrystallize.
(8) All compounds **1a–4a** were compared with the authentic samples for TLC, IR, NMR and melting point data.
(9) M.R.D. supported as NIH Trainee, 1973–1976.

A Convenient Synthesis of 1-Bromo-8-iodonaphthalene and 1,8-Dibromonaphthalene from 8-Bromo-1-naphthoic Acid

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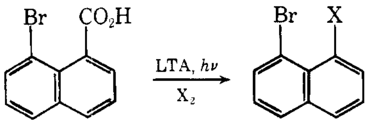
1,8-Dihalonaphthalenes, especially those containing bromine and/or iodine, are important intermediates for the preparation of naphthalene-based heterocycles and other naphthalene derivatives. Fieser and Seligman[2] prepared several 1,8-disubstituted naphthalenes from 1,8-diaminonaphthalene employing a modified stepwise diazotization procedure.[3] This method is time consuming and does not give satisfactory results.[4] Direct tetraazotization of 1,8-diaminonaphthalene is useful for preparing 1,8-diiodonaphthalene (1)[5] but does not give good yields of 1,8-dibromonaphthalene (2)[4] and is not a feasible route to mixed dihalonaphthalenes.

A synthesis of 2 using the Hunsdiecker reaction on 8-bromo-1-naphthoic acid (3) was reported[4] and 1-bromo-8-iodonaphthalene (4) has been prepared by treating 8-bromo-1-naphthoic acid with red mercuric oxide and iodine.[6a] For large scale preparations of these compounds both routes have disadvantages: the former requires expensive silver salts and the latter gives modest yields (28%).

Since our work requires that we have ready access to all three dihalonaphthalenes, 1, 2, and 4, we investigated all of the reported methods for making these compounds in order to find the most reliable and efficient routes. The diazotization procedures[2] for preparing 2 and 4 gave yields varying from 0 to 30%. These reactions are apparently very sensitive to the state of the catalyst. We were not successful in finding a way to make it consistently active.

Although we found the tetraazotization procedure[5] useful for preparing 1,[7] we could not extend this method to 2, an observation consistent with that made earlier.[4] Our efforts to improve the yields of the mercuration–iodination reaction[6a] to produce 4 were unsuccessful. When we substituted iodine monochloride for iodine we isolated no product from the reaction mixture.

We did find that lead tetraacetate (LTA) induced halodecarboxylation, a procedure usually inefficient for aromatic acids,[8] is a convenient route to both 2 and 4 from 3.



3

2, X = Br
4, X = I

We have found the yields consistently good for 4 (≥75%, isolated) using LTA, halogen, and 3. The yields of 2 run lower (~50%, isolated) but are still in the useful range.

Attempts to extend this method to making 1, 2, 3, and 8-iodonanaphthoic acid (5) from 1,8-naphthalenedicarboxylic acid (6) failed using pure benzene and pure tetrahydrofuran solvent systems.

Experimental Section

Melting points were determined on a Thomas-Hoover Mel-Temp melting point apparatus and are corrected. Infrared spectra were taken on a Perkin-Elmer Infracord 137 using pressed KBr pellets. NMR spectra were obtained from a Varian A60-A spectrometer in $CDCl_3$ with Me_4Si as internal standard. IR, NMR, and mass spectra of 4 and 2 are consistent with the assigned structures.

1-Bromo-8-iodonaphthalene (4). In a three-necked 1-L round-bottom flask equipped with heating mantle, reflux condenser, magnetic stirrer, and a syringe needle for bubbling N_2 through the solution were placed 750 mL of dry benzene and 14 g of 8-bromo-1-naphthoic acid.[9] This slurry was warmed to near reflux to dissolve 3. Nitrogen was bubbled through the solution and moist lead tetraacetate freshly made from 57 g of Pb_3O_4 in 98 mL of glacial acetic acid and 32 mL of acetic anhydride[10] was added to give a deep red solution. The solution was irradiated with a 275-W sunlamp and turned yellow after 5 min. Iodine was added in small portions with time allowed between additions for the iodine color to discharge. Large amounts of lead salts precipitated during the addition of the iodine. When the iodine color did not discharge after 15 min of irradiation, the reaction was assumed to be complete and the light was turned off. The red solution was cooled, filtered, and washed with saturated sodium thiosulfate solution. The resulting yellow benzene solution was dried with anhydrous $MgSO_4$ and filtered, and the solvent was removed in vacuo. The brown solid obtained was placed on a 10 × 5 cm column of alumina (Alcoa F-20, neutral, activated) and eluted with hexane as one large fraction. Removal of the hexane gave 13.6 g (75%) of a pale yellow solid, mp 92–93 °C (lit. mp[6] 91–92 °C). A second run on the same scale produced 13.7 g (76%) of 4.

1,8-Dibromonaphthalene (2). The procedure was the same as that for 4 with the exception that bromine was added in small portions by syringe. Six grams of 8-bromo-1-naphthoic acid (3) gave 4.5 g (66%) of a pale yellow solid after chromatography on alumina with hexane, mp 82–85 °C. Recrystallization from ethanol gave 3.4 g (50%) of an off-white solid, mp 104–105 °C.[6a,b] A second run on 4 g of 3 gave 1.8 g (40%) after recrystallization, mp 104–105 °C (lit. mp 109–110[2] and 106–108 °C[6]).

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Registry No.—**2,** 17135-74-9; **3,** 1729-99-3; **4,** 4044-58-0.

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