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Registry No.—**1**, 3240-34-4; **2**, 932-72-9; **4a**, 27126-76-7; **4b**, 61477-31-4; **4c**, 61477-32-5; **4d**, 61477-33-6; *p*-toluenesulfonic acid, 104-15-4; benzenesulfonic acid, 98-11-3; *p*-chlorobenzenesulfonic acid, 98-66-8; *p*-nitrobenzenesulfonic acid, 138-42-1; silver *p*-toluenesulfonate, 16836-95-6; silver benzenesulfonate, 39938-06-2; silver *p*-chlorobenzenesulfonate, 39938-10-8; silver *p*-nitrobenzenesulfonate, 39938-18-6; iodobenzene, 591-50-4.

References and Notes

(1) N. W. Alcock and T. C. Waddington, *J. Chem. Soc.*, 4103 (1963).
(2) O. Neiland and B. Karele, *J. Org. Chem. USSR (Engl. Transl.)*, **6**, 889 (1970).
(3) G. F. Koser, R. H. Wettach, J. M. Troup, and B. A. Frenz, *J. Org. Chem.*, **41**, 3609 (1976).

Improved Synthesis of 3-Methylphthalic Anhydride[1]

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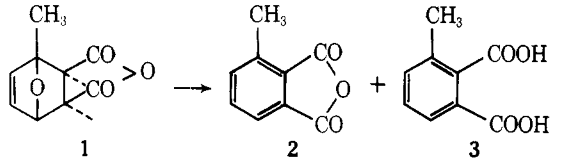
The Diels–Alder reaction of furans with maleic anhydride (MA) is known to occur in excellent yield in many cases.[3] However, the aromatization of these adducts to derivatives of phthalic anhydride is less well documented. In an early paper *exo-cis*-1-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (**1**), the adduct of 2-methylfuran and MA, **2**, was converted to 3-methylphthalic anhydride (**2**) by treatment with hydrogen bromide in acetic acid but no details or yields were given.[4]



1 2 3

In this laboratory, 3,6-dimethylphthalic anhydride was prepared in 45% yield[5] by adding the 2,5-dimethylfuran–MA adduct to 90% sulfuric acid at −6 to 0 °C. Similarly, 3-methylphthalic anhydride was prepared from 1 in 38% yield.[6] The adduct of 2-acetoxyfuran and MA was converted into 3-acetoxyphthalic anhydride in 57% yield by heating with acetic anhydride containing sulfuric acid.[7] In this paper we report on our efforts to improve the yield of **2** by treatment of **1** with acidic reagents. In addition to the isolation of **2**, we also examined the reaction mixtures for 3-methylphthalic acid (**3**) and other compounds, but the side products, when isolated, proved to be tars, except in one experiment (no. 5, Table I). No attempt was made to isolate highly water-soluble compounds.

Of the acidic reagents tried, 98% sulfuric acid proved the most promising. The best result (expt 2), a 66% yield, was obtained when the mixing of reagents was done at very low temperatures. In order to attain a low-temperature liquid medium with sulfuric acid a cosolvent, sulfolane, was needed. The desirability of having a low temperature may be explained by assuming that one reason for getting a low yield in these reactions is that an acid-catalyzed reversal of the Diels–Alder reaction[8,9] competes with acid-catalyzed dehydration to the desired product. This reversal of the Diels–Alder reaction is less important at lower temperatures and hence a higher yield of dehydration product results. In support of this concept, the fact that a 25% yield of 5-acetyl-2-methylfuran[10] was obtained in a BF_3–Ac_2O–AcOH medium (expt 5, Table I) is pertinent. This compound undoubtedly arises from acetylation of the 2-methylfuran formed by reversion of the Diels–Alder adduct to its components. In other acidic media used any 2-methylfuran formed was converted either into water-soluble products or tars.

Experimental Section[11]

***exo-cis*-1-Methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Anhydride (1).** In the best of several large-scale runs, 216 g (2.20 mol) of freshly distilled maleic anhydride was dissolved in 600 mL of dry ether freshly distilled from Grignard reagent.[12] To this solution 4 g of hydroquinone and 200 g (2.44 mol) of freshly distilled 2-methylfuran were added at room temperature. After 4 h the mixture was placed in a refrigerator overnight. The crystals (322 g, 81.3% based on MA) which had separated were collected and washed with an ether–petroleum ether mixture and melted at 80–81 °C. Further cooling of the combined filtrates yielded 48.6 g (12.3%) of **1**, mp 79–80 °C.[13] The total yield was thus 94.6% based on MA and 85% based on 2-methylfuran. In order to obtain such high yields it is important that all reactants and solvents be freshly distilled. As we never tried a run without hydroquinone we do not know if the presence of hydroquinone is necessary.

3-Methylphthalic Anhydride (2). The highest yields obtained are represented by expt 3, Table I. On a large scale 250 mL of concentrated H_2SO_4 (98%) was dissolved in 100 mL of freshly distilled sulfolane[14] and the solution was cooled to −55 °C (alcohol thermometer) with dry ice–isopropyl alcohol. Finely powdered, freshly

Table I. Conversion of 1 to 2 [a]

			Yield, %		
Expt	Acid medium	Conditions	2	3	Tar, other
1[a]	98% H_2SO_4	−20 to −10 °C, 4 h 25 °C, 1 h	38	0	0
2	85% H_2SO_4	0–26 °C, 2 h	1	25	0
3[a]	98% H_2SO_4 in sulfolane	−55 to −45 °C, 3 h −45 to 26 °C, 3 h	66	0	0
4[a]	HF (liq)	−78 to 26 °C, 24 h	30	5	65
5	BF_3, Ac_2O, HOAc	25 °C, 3 h	0	0	25[b]
6	80% H_3PO_4, 20% H_2SO_4	0–27 °C, 2 h	5	5	0
7	71% CH_3SO_3H, P_2O_5[c]	0–26 °C, 5 h	10	0	0
8	71% CH_3SO_3H	0–26 °C, 5 h	0	0	100[d]
9	Dry HCl in ether	0–25 °C, 3 h	0	0	100[d]

[a] The reactions were carried out in general with 5–10 g of **1** and appropriate volumes of the acidic reagents, e.g., 50–100 mL. All productive experiments were run in duplicate with excellent agreement of results. [b] 5-Acetyl-2-methylfuran. [c] 1 equiv of P_2O_5 added for the 29% of H_2O. [d] Starting material, **1**.

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.

References and Notes

(1) This work was supported by Grant GP-12445 from the National Science Foundation.
(2) Work done as undergraduate research problem.
(3) M. C. Kloetzel, "Organic Reactions", Vol. IV, Wiley, New York, N.Y., 1948, Chapter 1.
(4) M. G. Van Campen, Jr., and J. R. Johnson, *J. Am. Chem. Soc.*, **55**, 430 (1933).
(5) M. S. Newman and B. T. Lord, *J. Am. Chem. Soc.*, **66**, 733 (1944).
(6) M. S. Newman and S. Blum, *J. Med. Chem.*, **7**, 466 (1964).
(7) M. P. Cava, C. L. Wilson, and C. J. Williams, Jr., *J. Am. Chem. Soc.*, **78**, 2303 (1956).
(8) See P. Yates and P. Eaton, *J. Am. Chem. Soc.*, **82**, 4436 (1960), and references cited therein for acid catalysis of Diels–Alder reactions.
(9) For the reversibility of the Diels–Alder reaction involving furan and MA see R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **70**, 1161 (1948).
(10) M. W. Farrar and R. Levine, *J. Am. Chem. Soc.*, **72**, 3695 (1950).
(11) All melting points and boiling points are uncorrected.
(12) M. S. Newman, "An Advanced Organic Laboratory Course", Macmillan, New York, N.Y., 1972, p 110.
(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$_4$Si 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$_2$O 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$_2$SO$_4$) 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.

References and Notes

(1) E. Vedejs, *J. Am. Chem. Soc.*, **96**, 5944 (1974).
(2) H. Mimoun, I. Seree de Roeh, and L. Sajus, *Bull. Soc. Chim. Fr.*, 1481 (1969).
(3) H. Mimoun, I. Seree de Roeh, and L. Sajus, *Tetrahedron*, **26**, 37 (1970).
(4) S. L. Regen and G. M. Whitesides, *J. Organomet. Chem.*, **59**, 293 (1973).
(5) MoOPH was prepared according to the procedure of Mimoun (ref 2). We noted that while preparing the complex MoO$_5$–H$_2$O–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