2300), 276 (3000), 223 (14 100); IR ($CHCl_3$) λ_{max} 1680, 1644, 1590, 1315, 1110 cm^{-1}; NMR ($CDCl_3$) δ 3.92 (s, 3 H), 4.17–4.47 (m, 4 H), 6.19, 6.36, 6.65, 6.82 (AB q, J = 10 Hz, 2 H), 7.07–7.85 (m, 3 H); mass spectrum, m/e (relative intensity) 232.073 55 (M^+, 100), 204 (20), 187 (50), 76 (80), calcd for $C_{13}H_{12}O_4$ 232.073 39. Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.24; H, 5.17. Found: C, 67.26; H, 5.30.

The monoacetal failed to react with isoprene even in the presence of boron trifluoride etherate.

Hydrolysis of Monoacetal (2c). A solution of the monoacetal (**2c**; 0.043 g, 0.18 mmol) in tetrahydrofuran (10 mL) and 1 N hydrochloric acid (10 mL) was stirred at 60 °C for 12 h. The mixture was poured into saturated sodium hydrogen carbonate which was then extracted with ether several times. The combined ethereal extracts were dried and evaporated to give red crystals (0.047 g) which were dissolved in methylene chloride. This solution was passed through a short column of alumina by using methylene chloride as the eluent. Evaporation of the yellow eluate gave yellow crystals of 5-methoxy-1,4-naphthoquinone [**2b**; mp 188–189 °C; 0.030 g (86%)], identified by spectral comparison with an authentic sample.

4-(Ethylenedioxy)-5-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene (6). A mixture of the quinone acetal **2c** (1.21 g, 5.2 mmol) in ethyl acetate (50 mL) with 5% Rh/C (62 mg)[32] was shaken with H_2 (1 atm) for 1 h and was then filtered. The filtrate was evaporated to give yellow-brown crystals (1.26 g) that yielded from cyclohexane yellow crystals of **6**: mp 96–96.5 °C; 942 mg (77%); IR ($CHCl_3$) ν_{max} 1700, 1590 cm^{-1}; NMR ($CDCl_3$) δ 2.1–2.9 (m, 4 H), 3.8 (s, 3 H), 4.0–4.3 (m, 4 H), 7.0–7.8 (m, 3 H); UV (cyclohexane) λ 306 nm (ϵ 1640), 247 (3430), 238 (3510), 218 (12 270); mass spectrum, m/e (relative intensity) 234.088 90 (M^+, 60), 206 (25), 189 (10), 178 (100), calcd for $C_{13}H_{14}O_4$ 234.089 20.

Oxidation of 1b with TTN in Methanol/Trimethyl Orthoformate. A solution of 5-methoxy-1-naphthol (**1b**; 0.5 g, 2.9 mmol) in methanol/trimethyl orthoformate (1:1, 30 mL) was added dropwise to a stirred solution of TTN (2.5 g, 5.78 mmol) in methanol/trimethyl orthoformate (20 mL) at −78 °C. The stirred mixture was then allowed to warm to room temperature. Petroleum ether was added, and the solution was filtered. The filtrate was passed through a short alumina column which was eluted with petroleum ether. Evaporation of the petroleum ether solutions gave greenish brown crystals [mp 172–175 °C; 0.68 g (63%)] believed to be compound **2d** on the basis of the spectroscopic properties: IR ($CHCl_3$) ν_{max} 1670, 1630, 1570 cm^{-1}; NMR ($CDCl_3$) δ 3.1 (s, 6 H), 3.9 (s, 3 H), 6.5 (AB q, 2 H), 6.8–7.8 (m, 3 H); mass spectrum, m/e (relative intensity) 234 (M^+, 1.45), 203 (100), 188 (43).

Compound **2d** reacts with ethyl cyanoacetate but not isoprene. Attempts to repeat the preparation of **2d** were not successful.

Reaction of 2c with Methyl Malonate. The quinone monoacetal (**2c**; 0.136 g, 0.59 mmol) in dry methanol (10 mL) was added dropwise to a solution of methyl malonate (0.085 g, 0.64 mmol) and a catalytic amount of sodium methoxide in methanol (10 mL). The mixture was stirred overnight at room temperature and was then partitioned between ether (25 mL) and saturated ammonium chloride (50 mL). The aqueous layer was extracted twice more with ether. The combined ethereal extracts were dried and evaporated in vacuo to give oily white crystals (0.233 g). These crystallized from petroleum ether/ethyl acetate to give the 1,4-adduct **7** as colorless crystals: mp 131–133 °C; 0.173 g (80%); NMR ($CDCl_3$) δ 2.7–4.3 (overlapping m with s at 3.63 and 3.80, 17 H), 6.9–7.6 (m, 3 H); IR ($CHCl_3$) ν_{max} 1755, 1735, 1690 cm^{-1}; mass spectrum, m/e (relative intensity) 364.1157 (57), 305 (32), 233 (40), 178 (100), calcd for $C_{18}H_{20}O_8$ 364.1158.

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Registry No. **1a**, 83-56-7; **1b**, 3588-80-5; **2a**, 481-39-0; **2b**, 4923-61-9; **2c**, 74555-12-7; **2d**, 74555-13-8; **6**, 76741-85-0; **7**, 76741-86-1; TTN, 13746-98-0; 1-naphthol, 90-15-3; 1,4-naphthoquinone, 130-15-4; methyl malonate, 108-59-8.

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Aromatization of Arene 1,2-Oxides. 1-(Trimethylsilyl)benzene 1,2-Oxide

James E. Van Epp, Jr., Derek R. Boyd,[1] and Glenn A. Berchtold*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Aromatization of 1-(trimethylsilyl)benzene 1,2-oxide (1) affords a mixture of *o*-(trimethylsilyl)phenol and phenol, the ratio of which is pH dependent. Aromatization of [5-^{2}H]-1-(trimethylsilyl)benzene 1,2-oxide gave the following results. (1) At pH 1.1 or 7 all the deuterium label in *o*-(trimethylsilyl)phenol was para to the hydroxyl group. (2) At pH 1.1 the phenol formed was exclusively [4-^{2}H]phenol, but at pH 7 it was 70–75% [4-^{2}H]phenol and 25–30% [3-^{2}H]phenol. The pathway of the aromatization reaction is discussed.

Our interest in the pathway of aromatization of arene 1,2-oxides derives from their possible role as intermediates in the ortho hydroxylation of aromatic substrates in biological systems.[2] Many arene 1,2-oxides, although not involved in normal metabolism, are nonetheless of interest for further understanding of the effect of the 1-substituent in determining the course of the aromatization reaction. Interest in the influence of the 1-trimethylsilyl substituent in determining the regiospecificity of oxirane ring-opening of arene 1,2-oxides follows from the observations that, although cations β to silicon are stabilized by σ–π hyperconjugation and cations α to silicon are destabilized, acid-catalyzed reactions of (trimethylsilyl)oxiranes normally proceed by cleavage of the C–O bond adjacent to the trimethylsilyl substituent.[3] In a preliminary report[4] we described the preparation of 1-(trimethylsilyl)benzene oxide–oxepin (**1**) and the 2-methyl (**2**) and 4-methyl (**3**)

(1) Department of Chemistry, Queen's University of Belfast, Belfast BT9 5AG, Northern Ireland.

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Table I. Yield of 8 and 9 from Aromatization of 1

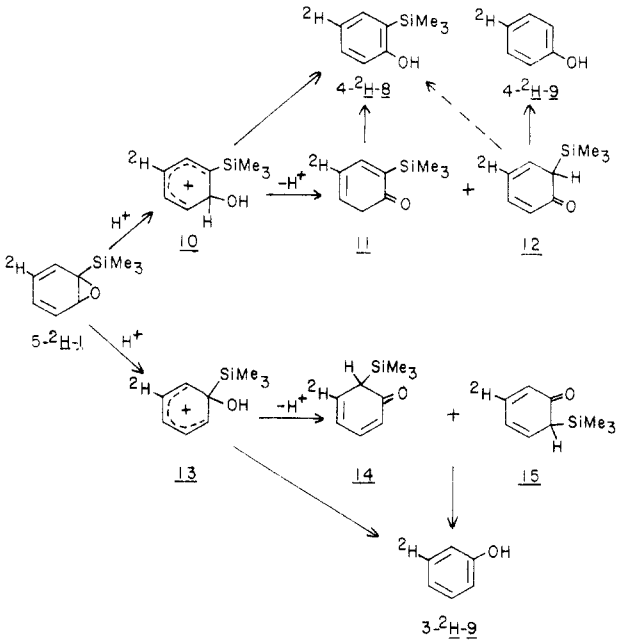
reacn conditions	%8 (obsd)[c]	%9 (obsd)[c]	max % 8 → 9 after aromatization
CF_3CO_2H (cat.)[a]	44	43	6.0
pH 0.1[b]	58	36	4.6
pH 1.1[b]	59	34	2.3
pH 4.0[b]	47	36	0
pH 7.0[b]	34	43	0
pH 10.0[b]	35	43	0

[a] In CH_2Cl_2. [b] In 3:1 MeOH/H_2O. [c] Percent yields were obtained by VPC analysis.

derivatives of 1 by conversion of dienes **4a–c** to dibromo epoxides **5–7** and subsequent base-catalyzed elimination of HBr to **1–3**, respectively (see Experimental Section). Products from aromatization of **1–3** under strongly acidic, nonaqueous conditions were reported.[4] Since trimethylsilyl substituents on an aromatic ring, including phenols,[5] are cleaved under the reaction time and acidic conditions described above, the aromatization of **1** was investigated under modified conditions at various pH's to determine the amounts of *o*-(trimethylsilyl)phenol (**8**) and phenol (**9**) formed directly from the aromatization reaction. Under strongly acidic conditions, **8** is not observed as a product if the reaction mixture is allowed to stand for several hours before analysis, but aromatization under these conditions is quite rapid. If the reaction mixture is neutralized ($KHCO_3$) within a few seconds (disappearance of oxepin color), the yields of **8** and **9** observed are as indicated in Table I, and no incorporation of deuterium into **8** or **9** is observed when **1** is aromatized at pH 1 in $^2H_2SO_4/^2H_2O$ followed by neutralization as soom as reaction is complete. When **8** is subjected to the same acidic reaction conditions for the same time period, the extent of desilylation of **8** to afford **9** is as follows: CF_3CO_2H (cat.), 12%; pH 0.1, 7.4%; pH 1.1, 3.8%. These results allow one to place an upper limit on the observed percent yield of **9** from desilylation of **8** after aromatization of **1** is complete (Table I). No observable desilylation of **8** occurs at pH 4, 7, or 10 over the time period required for complete aromatization of **1** (up to 19 days). From the data of Table I, it is clear that both **8** and **9** are formed during the aromatization of **1**, and the observed ratio of **8**:**9** and total yield of **8** + **9** decrease somewhat at higher pH in aqueous methanol.

Evidence for the pathway of aromatization of **1** was obtained from studies with [5-^{2}H]-**1** that was prepared from [5-^{2}H]-1,3-bis(trimethylsilyl)benzene (100% deuterium incorporation), obtained from [5-^{2}H]-1,3-dibromobenzene,[6] by the same procedure for the preparation of **1**. Aromatization of [5-^{2}H]-**1** in 3:1 MeOH/H_2O at pH 1.1 afforded [4-^{2}H]-**8** and [4-^{2}H]-**9** (Scheme I). That all of the deuterium was located at C-4 of the phenolic products was established from the ^{1}H NMR spectra. Aromatization at pH 1.1 must proceed solely through formation of cation **10** (and not **13**) with subsequent NIH shift of hydrogen to afford **11** and **12**. Formation of *o*-(trimethylsilyl)phenol ([4-^{2}H]-**8**) occurs by enolization of **11** (and perhaps **12**) and possibly also by direct loss of H^+ from **10**. Phenol is formed by nucleophilic displacement by solvent at the silicon atom of **12**.

Scheme I



Aromatization of [5-^{2}H]-**1** in 3:1 MeOH/H_2O at pH 7 afforded [4-^{2}H]-**8** (no ^{2}H at C-3 or C-5), and, consequently, the product arises exclusively by initial formation of cation **10**. The phenol formed at pH 7 was 70–75% [4-^{2}H]-**9** and 25–30% [3-^{2}H]-**9**. Therefore, some reaction at pH 7 occurs by initial formation of cation **13** that affords [3-^{2}H]-**9** directly through nucleophilic displacement at silicon by solvent. Alternatively, migration of the trimethylsilyl group[7] of **13** would afford **14** and **15** that are converted to [3-^{2}H]-**9** as described above for **12** → [4-^{2}H]-**9**. This latter pathway involving migration of the trimethylsilyl group of **13** may not be important, but if such a pathway is involved, then **12** cannot be an intermediate to [4-^{2}H]-**8** since no [3-^{2}H]-**8** and [5-^{2}H]-**8** are observed in the reaction at pH 7.

The increase in the ratio of **9**:**8** at higher pH is due to the change in mechanism where reaction involving cation **13** becomes significant.

Minor amounts of unidentified materials are observed in the reactions at higher pH. In view of the long reaction time at pH 7 and 10 (19 days for complete reaction), some side reactions occur involving nucleophilic addition of phenolic products to the starting material. Such reactions are not without precedent.[8,9]

Experimental Section

Melting points were determined with a Thomas-Hoover Unimelt apparatus and are corrected. ^{1}H NMR spectra were obtained at 60 and 250 or 270 MHz with Varian T-60 and Brüker FT spectrometers, respectively. Chemical shift values (δ) are reported in parts per million downfield from Me_4Si. Mass spectra were determined with a Varian MAT 44 instrument. Infrared spectra were obtained with a Perkin-Elmer Model 567 grating spectrophotometer. Ultraviolet spectra were obtained with a Cary Model 14 spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

1-(Trimethylsilyl)-1,4-cyclohexadiene (4a): from 1,3-bis(trimethylsilyl)benzene[10] (79% based on starting material con-

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sumed); bp 67 °C (20 mm) [lit.[10] bp 67 °C (20 mm)].

2-Methyl-1-(trimethylsilyl)-1,4-cyclohexadiene (4b): from 2,6-bis(trimethylsilyl)toluene[10] (25%); bp 65–75 °C (6 mm) [lit.[10] bp 75 °C (10 mm)].

4-Methyl-1-(trimethylsilyl)-1,4-cyclohexadiene (4c): from 4-(trimethylsilyl)toluene[10] (77%); bp 62–65 °C (5 mm) [lit.[10] bp 73 °C (9.5 mm)].

4,5-Dibromo-1-(trimethylsilyl)cyclohexene Oxide (5). To a stirring mixture of **4a** (50.8 g, 0.33 mol) and K_2CO_3 (32.3 g, 0.23 mol) in 600 mL of diethyl ether was added dropwise a solution of 85% *m*-chloroperoxybenzoic acid (74.8 g, 0.37 mol) in 800 mL of diethyl ether at a rate to maintain the temperature below 30 °C. The mixture was kept at room temperature for 24 h after addition was complete. The mixture was extracted with aqueous Na_2SO_3 and with aqueous Na_2CO_3, dried ($MgSO_4$) and concentrated in vacuo. Distillation of the residue through a spinning-band column afforded 27.5 g (49%) of 1-(trimethylsilyl)-1,4-cyclohexadiene 1,2-oxide: bp 81–84 °C (0.7 mm); ^1H NMR ($CDCl_3$) δ 0.24 (s, 9 H, Me_3Si), 2.27 (m, 4 H, 2 CH_2), 3.09 (br s, 1 H, epoxy H), 5.21 (br s, 2 H, vinyl H). Anal. Calcd for $C_9H_{16}OSi$: C, 64.42; H, 9.58. Found: C, 64.32; H, 9.77.

Bromine (1.12 g, 7 mmol) in 5 mL of 1:1 $CH_2Cl_2/CHCl_3$ was added dropwise to a solution of 1-(trimethylsilyl)-1,4-cyclohexadiene 1,2-oxide (0.84 g, 5 mmol) in 25 mL of 1:1 $CH_2Cl_2/CHCl_3$ at −78 °C with stirring. After 15 min the cooling bath was removed and the reaction was kept at room temperature for 2 h. The mixture was extracted with aqueous $Na_2S_2O_3$, dried ($MgSO_4$), and concentrated. Traces of solvent were removed under high vacuum to give an isomeric mixture of **5** (1.33 g, 81%) that was used without further purification. Although substantial decomposition occurs on distillation, an analytical sample was obtained: bp 95–97 °C (0.07 mm); ^1H NMR ($CDCl_3$) δ 0.07 (s, 9 H, Me_3Si), 2.2–3.4 (m, 4 H, 2 CH_2), 3.00 (m, 1 H, epoxy H), 3.9–4.6 (m, 2 H, CHBr). Anal. Calcd for $C_9H_{16}Br_2OSi$: C, 34.63; H, 5.17. Found: C, 34.60; H, 5.11.

1-(Trimethylsilyl)-2-methyl-4,5-dibromocyclohexene oxide (6) was prepared from **4b** by the same procedure for preparation of **5**. Epoxidation of **4b** afforded 1-(trimethylsilyl)-2-methyl-1,4-cyclohexadiene 1,2-oxide: 61%; bp 40–46 °C (0.6 mm, molecular distillation); ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H, Me_3Si), 1.34 (s, 3 H, CH_3), 2.37 (s, 4 H, 2 CH_2), 5.41 (s, 2 H, Vinyl H). Anal. Calcd for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95. Found: C, 65.26; H, 9.47.

Bromination of the epoxide gave **6**: 100%; bp 120 °C (0.02 mm); ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H, Me_3Si), 1.35 (s, 3 H, CH_3), 1.70–3.20 (m, 4 H, 2 CH_2), 3.90–6.50 (m, 2 H, CH Br). Anal. Calcd for $C_{10}H_{18}Br_2OSi$: C, 35.10; H, 5.30. Found: C, 35.22; H, 5.17.

1-(Trimethylsilyl)-4-methyl-4,5-dibromocyclohexene oxide (7) was prepared by bromination of **4c** followed by epoxidation. By use of a procedure similar to that for the preparation of **5**, 1-(trimethylsilyl)-4-methyl-4,5-dibromocyclohexene could be isolated and was contaminated with ca. 20% of the isomeric 1-methyl-4-(trimethylsilyl)-4,5-dibromocyclohexene: 38%; bp 80–90 °C (0.15 mm); ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H, Me_3Si), 1.89 (s, 3 H, CH_3), 2.14–3.59 (m, 4 H, 2 CH_2), 4.52 (m, 1 H, CHBr), 5.81 (m, 1 H, vinylic H).

Peroxytrifluoroacetic acid was generated from trifluoroacetic anhydride (22.35 g, 0.106 mol) and 3 mL of 90% hydrogen peroxide (ca. 3.75 g, 0.110 mol) in 10 mL of methylene chloride. Disodium hydrogen phosphate (45 g, 0.317 mol), the dibromo olefin (5.0 g, 0.015 mol), and methylene chloride (40 mL) were combined; the peracid was added dropwise, with stirring, to the mixture. The reaction was allowed to proceed at ambient temperature for 4 h and was extracted with aqueous Na_2SO_3 and aqueous Na_2CO_3. The extracts were dried ($MgSO_4$) and concentrated to give 5.0 g (95%) of crude product which was contaminated with impurities and suffered substantial decomposition on molecular distillation: bp ca. 80–100 °C (0.02 mm); ^1H NMR ($CDCl_3$) δ 0.08 (s, 9 H, Me_3Si), 1.83 (s, 3 H, CH_3), 2.11–2.91 (m, 4 H, 2 CH_2), 2.91–3.13 (m, 1 H, epoxy H), 4.21–4.81 (m, 1 H, CHBr).

1-(Trimethylsilyl)benzene oxide–oxepin (1). Dibromo epoxide **5** (8.25 g, 25.1 mmol) in THF (50 mL) was treated with DBN (6.26 g, 50.4 mmol) in THF (50 mL), and the mixture was stirred at ambient temperature for 24–36 h. The precipitate of DBN·HBr was removed by filtration and washed with THF. The combined THF filtrates were diluted with H_2O and extracted with diethyl ether. The ether extracts were dried ($MgSO_4$) and concentrated. Distillation through a spinning-band column was required to obtain **1** (20–35%) free of aromatic byproducts: bp 53–54 °C (4.5 mm); ^1H NMR ($CDCl_3$) δ 0.16 (s, 9 H, Me_3Si), 5.5-5.8 (m, 1 H, H_3), 5.8–6.1 (m, 2 H, H_2 and H_6), 6.1–6.5 (m, 2 H, H_4 and H_5); UV_{max} (isooctane) 302 nm (ϵ 1190); UV (MeOH) 297 nm (ϵ 1460); high-resolution mass spectrum, calcd for $C_9H_{14}OSi$ 166.08139, found 166.08148.[11]

Arene oxide **1** reacted with 4-methyl-1,2,4-triazoline-3,5-dione to afford, in quantitative yield, a crystalline adduct: mp 140–141 °C (benzene–pentane); ^1H NMR ($CDCl_3$) δ 0.20 (s, 9 H, Me_3Si), 2.95 (s, 3 H, MeN), 3.45 (d, 1 H, J = 4 Hz, epoxy H), 5.12 (m, 2 H, CHN), 6.01 (m, 2 H, vinyl H). Anal. Calcd for $C_{12}H_{17}N_3O_3Si$:C, 51.59; H, 6.13; N, 15.04. Found: C, 51.29; H, 6.22; N, 15.08.

1-(Trimethylsilyl)-2-methylbenzene oxide–oxepin (2) was prepared in 33% yield from **6** by the same procedure for the preparation of **1**: bp 40–50 °C (0.02 mm); ^1H NMR ($CDCl_3$) δ 0.17 (s, 9 H, Me_3Si), 1.87 (s, 3 H, CH_3), 5.31 (m, 1 H, H_3), 5.73 (m, 1 H, H_6), 5.95 (m, 2 H, H_4 and H_5); UV_{max} (isooctane) 323 nm (ϵ 1070); UV (MeOH) 317 nm (ϵ 1220); high-resolution mass spectrum, calcd for $C_{10}H_{16}OSi$ 180.09704, found 180.09630.[11]

Reaction of **2** with 4-methyl-1,2,4-triazoline-3,5-dione afforded, in quantitative yield, a crystalline adduct: mp 98–100 °C (pentane); ^1H NMR ($CDCl_3$) δ 0.07 (s, 9 H, Me_3Si), 2.13 (s, 3 H, MeC), 3.04 (s, 3 H, MeN), 4.54 (dd, 1 H, CHN), 5.18 (d, 1 H, vinyl H), 5.60 (d, 1 H, vinyl H), 6.50 (dd, 1 H, vinyl H); mass spectrum, *m/e* (relative intensity) 45 (39), 72 (39), 73 (100), 94 (51), 179 (47), 293 (34); high-resolution mass spectrum, calcd for $C_{13}H_{19}N_3O_3Si$ 293.11957, found 293.11919.[11]

1-(Trimethylsilyl)-4-methylbenzene oxide–oxepin (3) was prepared in 18% yield by the same procedure for the preparation of **1**: bp 30–55 °C (0.03 mm); ^1H NMR ($CDCl_3$) δ 0.13 (s, 9 H, Me_3Si), 1.82 (s, 3 H, CH_3), 5.30 (d, 1 H, H_3), 5.55–6.05 (m, 3 H, H_2, H_5, and H_6); UV_{max} (MeOH) 287 nm (ϵ 1050); high-resolution mass spectrum, calcd for $C_{10}H_{16}OSi$ 180.09704, found 180.09580.[11]

Arene oxide **3** reacted with 4-methyl-1,2,4-triazoline-3,5-dione to afford, in quantitative yield, a crystalline adduct: mp 155–156 °C (pentane); ^1H NMR ($CDCl_3$) δ 0.10 (s, 9 H, Me_3Si), 1.76 (s, 3 H, MeC), 2.85 (s, 3 H, MeN), 3.34 (d, 1 H, J = 4.5 Hz, epoxy H), 4.85 (m, 2 H, CHN), 5.3–5.6 (m, 1 H, vinyl H). Anal. Calcd for $C_{13}H_{19}N_3O_3Si$: C, 53.22; H, 6.53; N, 14.32. Found: C, 53.40; H, 6.62; N, 14.30.

[5-^{2}H]-1,3-Bis(trimethylsilyl)benzene. Mg turnings (21.5 g, 0.88 mol) were added to 500 mL of dry THF under N_2. A few crystals of I_2 were added, and [5-^{2}H]-1,3-dibromobenzene[6] (80.6 g, 0.34 mol) was added dropwise. The exothermic reaction was controlled with an ice bath. After addition was coomplete, the mixture was refluxed for 3 h and cooled, and chlorotrimethylsilane (95.9 g, 0.88 mol) was added gradually by a syringe. The mixture was refluxed for 20 h, cooled, quenched with water, and acidified with dilute HCl. The mixture was extracted with ether, and the extracts were dried ($MgSO_4$) and concentrated. Fractional distillation afforded the product (54.9 g, 72%): bp 100–101 °C (20 mm) [lit.[12] bp 112 °C (22 mm) for the undeuterated compound]; ^1H NMR (CCl_4) δ 0.30 (s, 18 H, Me_3Si), 7.52 (m, 2 H, H_4 and H_6), 7.65 (m, 1 H, H_2). The product contained 99+% deuterium at C-5.

[5-^{2}H]-1-(Trimethylsilyl)benzene oxide ([5-^{2}H]-1) was prepared from [5-^{2}H]-1,3-bis(trimethylsilyl)benzene by the same procedure described above for the preparation of **1**. The product contained 99+% deuterium at C-5: ^1H NMR (CD_2Cl_2/CCl_4, 250 MHz) δ 0.19 (s, 9 H, Me_3Si), 5.59 (t, J = 5.5 Hz, 1 H, H_3), 5.82 (d, J = 5.5 Hz, 1 H, H_2), 5.91 (br s, 1 H, H_6), 6.22 (br d, J = 5.5 Hz, 1 H, H_4).

Trifluoroacetic Acid Catalyzed Aromatization of 1–3.

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(11) High-resolution mass spectra were provided by the facility supported by National Institutes of Health Grant RR00317 (principal investigator Professor K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources.

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When the arene oxides were dissolved in CF_3CO_2H or $CDCl_3$ containing a few drops of CF_3CO_2H and kept at room temperature for several hours, 1 and 2 afforded phenol and *p*-cresol, respectively, in quantitative yield. Under the same conditions 3 gave in quantitative yield a 45:55 mixture of *m*- and *p*-cresol. The phenolic products were characterized by comparison of IR and ^1H NMR spectra with those of authentic samples.

Aromatization of 1 in CH_2Cl_2 containing a few drops of CF_3CO_2H with quenching by addition of $KHCO_3$ as soon as the yellow oxepin color disappeared (several seconds) gave 8 and 9 as indicated in Table I. The ratio of products was determined by VPC as described below.

Aromatization of 1 in Aqueous Methanol. Arene oxide 1 (40 mg) and 2-isopropylphenol (20 mg, internal standard for VPC analysis) were dissolved in 3 mL of CH_3OH and to the solution was added 1 mL of water at pH 0.1 (HCl), 1.1 (HCl), 4.0 (biphthalate buffer), 7.0 (phosphate buffer), or 10.0 (carbonate–borate) buffer. The more acidic reactions (pH 0.1 and 1.1) were quenched with $KHCO_3$ as soon as the yellow color of oxepin disappeared (several seconds). The reactions at pH 4, 7, and 10 were kept at room temperature until 1 was completely consumed (up to 19 days). Control experiments established that product 8 did not desilylate under the reaction conditions at pH 4, 7, and 10. The yields of 8 and 9 were established by VPC analysis (3% SE-30 on Chromosorb Q column at 90 °C) with standardization of response factors of authentic samples relative to 2-isopropylphenol as the internal standard. The results are reported in Table I.

Aromatization of [5-^2H]-1 in Aqueous Methanol. Arene oxide [5-^2H]-1 (300 mg) was dissolved in 1.5 mL of CH_3OH and 0.5 mL of aqueous HCl (pH 1.1) was added. Upon discharge of the yellow color of the arene oxide (several seconds), $KHCO_3$ was added. The mixture was brought to neutrality with aqueous NH_4Cl and extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$) and concentrated. Phenol and *o*-(trimethylsilyl)phenol were isolated by preparative thin-layer chromatography (silica gel, 4:1 petroleum ether–Et_2O) of the residue.

The reaction at pH 7 (0.5 mL of phosphate buffer) was performed in the same manner except that the reaction was not quenched with $KHCO_3$.

That no loss of deuterium from the reaction products occurred by exchange was established by the fact that neither [4-^2H]phenol, prepared by demethylation of [4-^2H]anisole[12] with BBr_3, nor [4,6-^2H]-(2-trimethylsilyl)phenol exchanged any deuterium label under the reaction conditions at pH 7. In addition, no evidence of exchange was observed in the 250-MHz ^1H NMR spectra of the phenolic products obtained in the aromatization of [5-^2H]-1a at either pH 1.1 or 7.

The position of deuterium in the products was established by comparison of the 250-MHz ^1H NMR spectra with those of the unlabeled materials. For unlabeled 8: ^1H NMR (CD_2Cl_2/CCl_4) δ 0.28 (s, 9 H, Me_3Si), 4.82 (s, 1 H, OH), 6.62 (d, $J_{5,6}$ = 8.3 Hz, 1 H, H_6), 6.86 (t, $J_{3,4} = J_{4,5}$ = 7.5 Hz, 1 H, H_4), 7.18 (d of t, $J_{3,5}$ = 1.7 Hz, 1 H, H_5), 730 (d of d, 1 H, H_3). Absorption for H_4 and $J_{3,4}$ and $J_{4,5}$ were totally absent from the spectrum of [4-^2H]-8 obtained from aromatization of [5-^2H]-1a at pH 1.1 and 7. For unlabeled 9: ^1H NMR (CD_2Cl_2/CCl_4) δ 5.01 (OH), 6.79 (H_2, H_6), 6.90 (H_4), 7.21 (H_3, H_5). Phenol from aromatization of [5-^2H]-1a at pH 1.1 had all the deuterium label at C-4 (adsorption at 6.90 ppm totally absent) and from aromatization at pH 7 had 70–75% deuterium at C-4 and 25–30% deuterium at C-3 (from integration of aromatic absorption).

***o*-(Trimethylsilyl)phenol (8)** was prepared as previously reported[13] with modifications. *o*-Bromophenol (5.19 g, 0.03 mol) was dissolved in dry THF (50 mL). To the solution was added triethylamine (4.04 g, 0.04 mol) followed by trimethylcholorosilane (3.47 g, 0.032 mol). Immediate decolorization was apparent (yellow → colorless) with precipitation of triethylamine hydrochloride. The reaction was stirred briefly at room temperature and rapidly filtered. Suction of air through the filter cake regenerated the yellow color in the filtrate. An additional portion of trimethylcholorosilane (3.47 g, 0.032 mol) was added to the filtrate followed by magnesium turnings (0.78 g, 0.032 mol). Upon catalysis with 1,2-dibromoethane, an exothermic reaction resulted. Reflux was maintained for 18 h after which the cooled reaction mixture was quenched with aqueous NH_4Cl and extracted with diethyl ether. The extracts were dried ($MgSO_4$) and concentrated. Vacuum distillation gave 4.88 g (68%) of *O,o*-bis(trimethylsilyl)phenol, bp 100–104 °C (20 mm) [lit.[14] 128 °C (25 mm)]. Since treatment with dilute HCl gave little *O*-desilylation and could potentially desilylate the ring, the method of Copper[15] was utilized for removal of the *O*-trimethylsilyl group. Treatment of *O,o*-bis(trimethylsilyl)phenol (4.88 g, 20.5 mmol) with 2.5 N sodium methoxide in methanol (50 mL) gave immediate O-desilylation at room temperature. The reaction was stirred and neutralized with excess aqueous NH_4Cl. The product was extracted with diethyl ether, and the extracts were dried ($MgSO_4$) and concentrated. Distillation afforded *o*-(trimethylsilyl)phenol: 2.82 g (83%); bp 100–105 °C (20 mm) [lit.[15] 109–110 °C (25 mm)].

[4,6-$^2H_2$]-2-(Trimethylsilyl)phenol. Treatment of *o*-(trimethylsilyl)phenol with NaOD in refluxing D_2O resulted in extensive desilylation; therefore, direct exchange was impractical. [2,4,6-^2H]Phenol was prepared with ~90% deuterium incorporation by twofold treatment with NaOD in refluxing D_2O (1.15 g, 0.05 mol of sodium dissolved in 50 mL D_2O for exchange of 9.4 g (0.10 mol) of phenol). The procedure of Pearson[16] was utilized for ortho bromination of phenol for preparation of [4,6-^2H]-2-bromophenol: 28%; bp 91–94 °C (25 mm) [lit.[15] bp 186–195 °C]. However, the product suffered some H/D exchange and was contaminated with [4-^2H]-2,6-dibromophenol. The [4,6-^2H]-2-bromophenol (4.37 g, 0.025 mol), which had lost some deuterium incorporation, was taken up in CH_2Cl_2 and shaken with D_2O to exchange the hydroxyl proton. The solvent was evaporated from the organic phase and the residue dissolved in a solution of sodium (0.29 g, 0.0125 mol) in D_2O (25 mL) and refluxed under nitrogen for 4 days. The cooled mixture was then neutralized with aqueous NH_4Cl and extracted with ether. The extracts were dried ($MgSO_4$) and concentrated. Vacuum distillation gave 3.68 g (84%) of [4,6-^2H]-2-bromophenol, bp 90–93 °C (25 mm), with near quantitative deuterium incorporation. It was contaminated with ca. 20% of [4-^2H]-2,6-dibromophenol. The material was subjected to silylation as in the preparation of 8 with the following modifications. The reaction was diluted with D_2O before quenching with aqueous NH_4Cl and O-desilylation was achieved with CH_3ONa in CH_3OD. Since vacuum distillation was unsuccessful in separating [2,4,6-^2H]phenol from [4,6-^2H]-2-(trimethylsilyl)-phenol, a pure sample of the latter was obtained by preparative TLC (silica, 4:1 petroleum ether (bp 40–60 °C)/diethyl ether): ca. 40% based on 80% purity of starting [4,6-^2H]-2-bromophenol; ^1H NMR (250 MHz, CD_2Cl_2/CCl_4) δ 0.28 (s, 9 H, Me_3Si), 4.88 (s, 1 H, OH), 7.19 (s, 1 H, H_5), 7.32 (s, 1 H, H_3).

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Registry No. 1, 69616-44-0; [5-^2H]-1, 76684-25-8; 2, 69616-45-1; 3, 69616-46-2; 4a, 54380-43-7; 4b, 55861-02-4; 4c, 55861-01-3; 5, 69616-51-9; 6, 69616-41-7; 7, 69616-43-9; 8, 15288-53-6; 9, 108-95-2; 1,3-bis(trimethylsilyl)benzene, 2060-89-1; 2,6-bis(trimethylsilyl)-toluene, 31825-45-3; 4-(trimethylsilyl)toluene, 3728-43-6; 1-(trimethylsilyl)-1,4-cyclohexadiene 1,2-oxide, 69616-39-3; 1-(trimethylsilyl)-2-methyl-1,4-cyclohexadiene 1,2-oxide, 69616-40-6; 1-(trimethylsilyl)-4-methyl-4,5-dibromocyclohexene, 76684-26-9; 1-methyl-4-(trimethylsilyl)-4,5-dibromocyclohexene, 76684-27-0; 4-methyl-1,2,4-triazoline-3,5-dione, 13274-43-6; [5-^2H]-1,3-bis(trimethylsilyl)benzene, 76684-28-1; [4,6-^2H]-2-(trimethylsilyl)phenol, 76684-29-2; *o*-bromophenol, 95-56-7; *O,o*-bis(trimethylsilyl)phenol, 18036-83-4; *p*-cresol, 106-44-5; *m*-cresol, 108-39-4; [2,4,6-^2H]phenol, 7329-50-2; [4,6-^3H]-2-bromophenol, 76684-30-5; phenol, 108-95-2.

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