used without purification in the next step. *o*-Dichlorobenzene (600 ml) was added to the crude **2** and the solution was refluxed for 4 hr. The volume was reduced to 250 ml and then diluted with hexane (200 ml). Acid **3** precipitated on standing. It was combined with further material obtained by additional reductions in volume and dilutions with hexane: 32 g, 73.4%; mp 180–185°, ir 3.00–4.50, 5.98 (COOH), 6.25 (C═C), 7.09, 8.14, 8.40, 10.99 μm; NMR, acid H indistinguishable,[8] 2.95 q (5a, 8a-H's, AB, J = 12 Hz), 2.8–1.2 m (all other H's). The analytical sample was produced upon recrystallization from methanol, mp 225–226°.

Anal. Calcd for $C_{12}H_{10}O_2Cl_4$: C, 43.94; H, 3.07. Found: C, 44.19; H, 3.11.

***ar*-Tetrachlorobenzonorbornene-*endo*-2-carboxylic Acid (4).** Crude acid **3** (32 g, 97.6 mmol) was added to chlorobenzene (160 ml) containing bromine (6.4 ml). The solution was refluxed for 4 hr, carefully decanted from ca. 0.5 ml of an immiscible tarry layer, and cooled. The acid **4** that precipitated was collected and combined with further crops obtained by evaporation and trituration with hexane: 23.8 g, 74.8%; mp 166–170°; ir 3.00–4.50, 5.92 (COOH), 7.06, 7.35, 7.79, 8.16, 8.26 μm; NMR, acid H indistinguishable,[8] 3.78 m, 3.67 m (H-1, 4), 2.5–1.2 m (all other H's). The analytical sample was obtained by recrystallization from *n*-octane, mp 215–216°.

Anal. Calcd for $C_{12}H_8O_2Cl_4$: C, 44.20; H, 2.48. Found: C, 44.18; H, 2.54.

Benzonorbornene-*endo*-2-carboxylic Acid (5). Crude acid **4** (19.6 g, 60 mmol), potassium hydroxide (85% material, 135 g), and water (1.36 l.) were stirred in a large flask while Raney nickel alloy (Alfa, 83.9 g) was added in portions over a 1.5-hr period. Considerable foaming occurred. After 3 hr the mixture was filtered and the residual solid was washed thoroughly with water. The washings were added to the original filtrate and the combined solution was acidified with hydrochloric acid (Congo Red endpoint). Extraction with ether several times then followed. Removal of the ether left crude acid **5**: 7.7 g, 68.3%; mp 127–129°; ir and NMR spectra identical with those reported. The analytical sample was obtained from hexane, mp 130–131°, and the mixture melting point with material obtained otherwise[2] was undepressed.

Methyl Benzonorbornane-*endo*-2-carboxylate (6). Acid **5** (6.4 g, 34 mmol) was dissolved in hexamethylphosphoramide (85 ml) containing sodium hydroxide (8 ml of a 25% aqueous solution). Methyl iodide (19.3 g, 0.136 mol) was added and the solution was stirred at 25° for 5 hr.[9] Hydrochloric acid (5%, 170 ml) was added and the solution was extracted with ether several times. The ether extracts were washed with aqueous sodium bisulfite and dried (Na_2SO_4). Removal of the ether left quite pure ester **6**: 5.8 g, 85%; m/e 202 (parent), retro-Diels–Alder fragments at 116 (base peak, isoindene), 115 (indene cation), 87 [$CH_2{=}CHC({=}^+OH)OCH_3$, as expected].[10] The ester was chromatographed on silicone gum rubber column (10% SE-52 on Chromosorb W) at 180°. No exo ester was present (checked with authentic sample) and the retention time of **6** was identical (by coinjection) with **6** made otherwise.[2] Also, the ir and NMR spectra of the two samples were identical and showed no trace of any exo impurity.

Registry No.—**1**, 55606-62-7; **3**, 55606-63-8; **4**, 55606-64-9; **5**, 54274-40-7; **6**, 54164-81-7; 5,5-dimethoxytetrachlorocyclopentadiene, 2207-27-4; norbornene-*endo*-2-carboxylic acid, 1195-12-6; *o*-dichlorobenzene, 95-50-1.

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(8) We have routinely experienced difficulty finding the acid proton in these compounds in Me_2SO-d_6 solvent. It is possible that these acids promote exchange even in this solvent.

(9) The method of J. E. Shaw et al., *Tetrahedron Lett.*, 688 (1973).

(10) Retro-Diels-Alder fragmentation (by several pathways) is the major source of MS peaks for norbornyl and benzonorbornenyl compounds. Cf. T. A. Eggelte and N. M. M. Nibbering, *J. Chem. Soc., Perkin Trans. 2*, 605 (1974); S. J. Cristol and G. Nachtigall, *J. Org. Chem.*, **32**, 3727 (1967); S. J. Cristol and A. L. Noreen, *J. Am. Chem. Soc.*, **91**, 3969 (1969); and ref 4.

Fluorinated Hydroquinones

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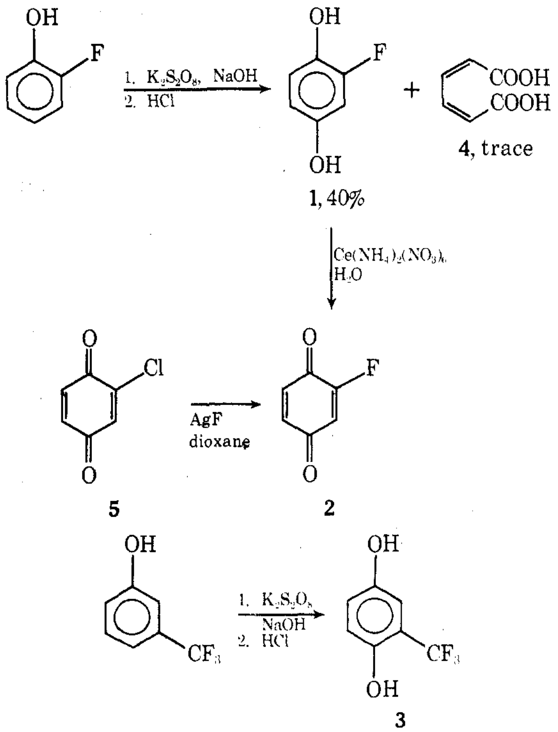
The fluorinated hydroquinones and benzoquinones possess interesting biological[1–3] and chemical[4–9] properties. Although some properties[2,3] of fluorohydroquinone (**1**) have been described, its preparation and spectroscopic characterization have not been detailed. A multistep preparation of fluorobenzoquinone (**2**) has been reported,[9] but its characterization was limited to elemental analysis. We now report simple preparations from commercially available starting materials of **1**, **2**, and trifluoromethylhydroquinone (**3**),[10] and polarographic half-wave potentials for oxidation of **1** and **3**.

Fluorohydroquinone (**1**) was prepared in 40% yield by oxidation of *o*-fluorophenol with potassium persulfate[11] in aqueous alkali, followed by hydrolysis of the intermediate *p*-hydroxyphenyl potassium sulfate with dilute HCl. The compound, a white solid, mp 124–126°, was isolated by silica gel chromatography and recrystallization from chloroform. In addition to **1** and ca. 35% recovered *o*-fluorophenol, a small amount of *cis,cis*-2,4-hexadienedioic acid (**4**) was obtained from the reaction, possibly due to oxidation of *o*-hydroquinone derived from displacement of fluoride in the starting phenol by OH.

In a similar fashion, oxidation of *m*-hydroxybenzotrifluoride with potassium persulfate afforded trifluoromethylhydroquinone (**3**) in 6% yield together with 40% recovered phenol. The extremely low yield of product may be due in part to steric hindrance to attack of the persulfate anion by the bulky trifluoromethyl group.



Fluorobenzoquinone (**2**) was obtained as bright yellow crystals from oxidation of **1** with ceric ammonium nitrate[12] in water, followed by sublimation. The compound was extremely sensitive to base; a black tarry precipitate formed

Table I
$E_{1/2}$ for Monosubstituted Hydroquinones[a]

Substituent	$E_{1/2}$[b]
H	+0.060
Cl	+0.065
F	+0.050
CF_3	+0.133

[a] Aqueous solution, 0.10 *M* NaH_2PO_4 buffer, pH 6.5. [b] Vs. SCE.

instantly on adding 5% aqueous $NaHCO_3$ to an ethanolic solution of **2**.

The reported[13] synthesis of tetrafluorobenzoquinone from the tetrachloro derivative and potassium fluoride prompted attempts to convert chlorobenzoquinone (**5**) to **2** by this method. However, heating **5** neat with KF or in benzene or acetonitrile solution with KF solubilized with 18-crown-6[14] afforded only tars; no **2** was detected by GLC after complete disappearance of **5**. Treatment of **5** (7.2 g) with 2 equiv of silver fluoride in dioxane at 200° gave a dark oil from which 2.8 g of a 42:58 mixture (by GLC) of **2** and **5** could be isolated by silica gel chromatography.

The polarographic behavior of substituted hydroquinones has been extensively investigated.[15] Since little data are available on the effects of fluorine substitution, we have determined the polarographic half-wave potentials for **1** and **3**. At pH 6.5 in aqueous phosphate buffer, the compounds exhibited clean, reversible two-electron oxidation; at higher pH, erratic results were obtained owing to rapid base-catalyzed destruction of the corresponding quinones. The measured values of $E_{1/2}$ for **1**, **3**, and related compounds are given in Table I. The data indicate little effect on $E_{1/2}$ by monohalo substitution, presumably owing to a balancing of the electron-withdrawing inductive and electron-donating resonance effects of these substituents.[16] For the trifluoromethyl derivative, the strong electron-withdrawing effect[16] causes a significant increase in oxidation potential. A dependence of $E_{1/2}$ for monosubstituted quinones on both the inductive and resonance effects of the substituent has been previously noted.[17]

Experimental Section

General. *o*-Fluorophenol (PCR, Inc.), potassium persulfate (Fisher Scientific), ceric ammonium nitrate (Fisher), potassium fluoride (MCB, anhydrous), and silver fluoride (Ozark-Mahoning) were reagent grade and used as received. Chlorohydroquinone (Eastman) was recrystallized from chloroform. *m*-Hydroxybenzotrifluoride (Pierce Chemical Co.) was distilled before use, bp 67° (6 mm). Acetonitrile and dioxane were anhydrous, reagent grade and were used directly from unopened bottles. Proton NMR spectra were run on a Varian A-60 instrument in the indicated solvents. Fluorine NMR spectra were run at 94.1 MHz on a Varian XL-100 instrument in the indicated solvents using F-11 as internal standard. GLC analyses were performed on a Hewlett-Packard 5700 instrument with thermal conductivity detector using a 10 ft × 0.25 in. 10% SE-30 column at 140°. Melting points were measured on a Thomas-Hoover melting point apparatus and are corrected.

Fluorohydroquinone (1). *o*-Fluorophenol (11.3 g, 0.100 mol) was dissolved in 400 ml of 6% aqueous NaOH. Solid potassium persulfate (27 g, 0.10 mol) was added to this stirred solution in several portions over 10 min. The dark mixture was stirred overnight at room temperature, then concentrated to ca. ⅓ its original volume on the rotary evaporator. The solution was neutralized with concentrated HCl and extracted once with 200 ml of ether. The aqueous solution was acidified with 100 ml of concentrated HCl, boiled for 1 hr, then concentrated to ca. 50 ml on the rotary evaporator. Addition of 200 ml of acetone precipitated the inorganic salts, which were removed by filtration. The filtrate was taken to dryness on the rotary evaporator and the dark residue, dissolved in acetone, was added to 15 g of silica gel. The solvent was removed and the material was added to a column of 100 g of silica gel packed in hexane. The column was eluted with 10% acetonitrile in chloroform, taking 75-ml fractions. Fractions 5–20 contained 5.3 g (41%) of product, showing a single spot on TLC. Further purification could be effected by dissolving the material in boiling chloroform (60 ml/g), concentrating the solution to ca. ⅓ its original volume, and cooling in an ice bath to give white plates: mp 122–123°; ir ($CHCl_3$) 3600 (s), 3300 (m), 1615 (m), 1520 cm^{-1} (s); proton NMR (Me_2SO-d_6) δ 6.23–6.97 (3 H, m), 8.97 (2 H, s); fluorine NMR (from F-11, Me_2SO-d_6) −134.3 ppm (m); mass spectrum, calcd for $C_6H_5O_2F$, *m/e* 128.0273; found, *m/e* 128.0259.

Anal. Calcd for $C_6H_5O_2F$: C, 56.26; H, 3.93. Found: C, 56.44; H, 4.03. The ether extract of the aqueous reaction solution was concentrated to an oil (4.0 g) which was identified as mostly unreacted *o*-fluorophenol by its NMR spectrum (δ 6.6–7.3, complex multiplet). A small amount of white solid was noted in the oil. Crystallization of the material from 30 ml of acetone gave 0.2 g of white crystals, identified as *cis,cis*-2,4-hexadienedioic acid: mp 199° (lit.[18] mp 194–195°); NMR (Me_2SO-d_6) δ 5.97 (2 H, doubled doublet, J_{12} = 7.8, J_{13} = 2.2 Hz), 7.72 (2 H, doubled doublet, J_{12} = 7.8, J_{13} = 2.2 Hz), 11.0 (2 H, broad singlet); mass spectrum, calcd for $C_6H_6O_4$, *m/e* 142.0266; found, *m/e* 142.0260.

Fluorobenzoquinone (2). Fluorohydroquinone (3.0 g, 0.023 mol) was added to a solution of 26 g (0.046 mol) of ceric ammonium nitrate in 150 ml of water. After stirring for 1 hr at room temperature the solution was extracted with 3 × 100 ml of ether. The combined ether extracts were dried ($MgSO_4$) and concentrated on the rotary evaporator. The residue (2.3 g) was sublimed at 50° (0.5 mm) to give 2.2 g (78%) of bright yellow crystals: mp 78–79°; ir ($CHCl_3$) 3060 (m), 1695 (s), 1675 (s), 1605 (m), 1380 (w), 1350 (s), 1305 (s), 1290 (sh), 1230 (w), 1195 (s), 1165 (m), 1090 (s), 890 (s), 835 cm^{-1} (m); proton NMR ($CDCl_3$) δ 6.48 (1 H, doublet with fine structure), 6.85 (2 H, m); fluorine NMR (from F-11, $CDCl_3$) −112.3 ppm (m).

Anal. Calcd. for $C_6H_3O_2F$: C, 57.15; H, 2.40; F, 15.08. Found: C, 56.87; H, 2.44; F, 15.10.

Reaction of Chlorobenzoquinone with Silver(I) Fluoride. A mixture of 7.20 g (0.050 mol) of chlorobenzoquinone, 12.7 g (0.100 mol) of silver fluoride, and 40 ml of dioxane was heated under N_2 in a pressure bomb at 200° for 4 hr. After cooling to room temperature, the contents of the bomb were filtered and the filtrate was concentrated on the rotary evaporator to a dark oil (6.9 g). The oil was chromatographed on silica gel, eluting with chloroform. Fractions showing quinone by TLC (silica plates) were combined and concentrated to a yellow solid. GLC of this material showed a 42:58 mixture of fluorobenzoquinone and chlorobenzoquinone.

Trifluoromethylhydroquinone (3). *m*-Hydroxybenzotrifluoride (16.2 g, 0.100 mol) was dissolved in 350 ml of H_2O and 50 ml of 50% aqueous NaOH. Solid potassium persulfate (27 g, 0.10 mol) was added in portions over 10 min. The resulting mixture was stirred overnight at room temperature. The solution was concentrated to ca. ⅓ its original volume on the rotary evaporator, neutralized with concentrated HCl, and extracted with 200 ml of ether. The aqueous solution was acidified with an additional 100 ml of concentrated HCl and boiled for 1 hr. After cooling to room temperature, the solution was concentrated to ca. 50 ml on the rotary evaporator. Addition of 200 ml of acetone precipitated the inorganic salts, which were removed by filtration. The filtrate was concentrated to a black oil on the rotary evaporator. The residue was dissolved in 600 ml of ether, dried over $MgSO_4$ and concentrated to a black oil (5.5 g). The material was dissolved in acetone and added to 15 g of silica gel. The solvent was removed and the material was added to a column of 100 g of silica gel packed in chloroform. The column was eluted with 10% acetonitrile in chloroform; 50-ml fractions were taken. Fractions 10–16, showing a single spot on TLC, were combined and concentrated to a red solid. Trituration with chloroform and drying on the vacuum pump gave 1.0 g of white crystals: mp 106–107° (lit.[10] mp 109°); proton NMR (acetone-d_6) δ 6.9–7.1 (3 H, m), 8.32 (2 H, s); fluorine NMR (from F-11, acetone-d_6) −62.0 ppm (s); ir (KBr) 3350 (s), 1640 (w), 1610 (w), 1515 (s), 1490 (m), 1480 (m), 1380 (s), 1320 (s), 1265 (m), 1255 (m), 1220 (m), 1200 (s), 1170 (m), 1130 (s), 1050 cm^{-1} (s); mass spectrum, calcd for $C_7H_5O_2F_3$, *m/e* 178.0241; found, *m/e* 178.0238. The ether extract of the original aqueous solution was dried ($MgSO_4$) and concentrated on the rotary evaporator to a dark oil. Distillation of the oil gave 6.5 g of unreacted *m*-hydroxybenzotrifluoride, bp 67° (6 mm).

Registry No.—**1**, 55660-73-6; **2**, 367-28-2; **3**, 577-10-6; **4**, 1119-72-8; **5**, 695-99-8; *o*-fluorophenol, 367-12-4; potassium persulfate, 7727-21-1; ceric ammonium nitrate, 16774-21-3; silver(I) fluoride, 7775-41-9; *m*-hydroxybenzotrifluoride, 98-17-9.

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Hydration of *p*-Nitrobenzaldehyde[1a]

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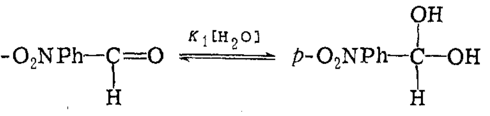
Although measurable hydration in neutral solution has been observed by Laviron, Troncin, and Tirouflet[2] for *o*-nitrobenzaldehyde and by Greenzaid[3] for 4-trimethylammoniobenzaldehyde iodide, it has been assumed[3,4] that the equilibrium constant, K_1, for this hydration reaction (eq 1)



$$p\text{-}O_2NPh-\underset{H}{C}=O \xrightleftharpoons{K_1[H_2O]} p\text{-}O_2NPh-\overset{OH}{\underset{H}{C}}-OH \tag{1}$$

of *p*-nitrobenzaldehyde is negligibly small, and to the author's knowledge no experimental evidence supporting a significant extent of hydration of this aldehyde in neutral or weakly acidic aqueous solution has previously been reported. Several recent observations in this laboratory indicate that the value of $K_1[H_2O]$, although small, is measurable and has an approximate value of 0.25 ± 0.1 at 25°, corresponding to approximately 20% hydration of the aldehyde. This finding means that a small but significant correction of observed rate and equilibrium constants for reactions of *p*-nitrobenzaldehyde is required in kinetic studies, especially when this aldehyde is compared with other, less significantly hydrated, substituted benzaldehydes in structure–reactivity correlations.

The following three experimental observations provide strong qualitative evidence that *p*-nitrobenzaldehyde is significantly hydrated in neutral aqueous solution, and are consistent with an approximate value for $K_1[H_2O]$ of 0.25 ± 0.1.

(1) Upon addition of a sample of *p*-nitrobenzaldehyde in acetonitrile solution to 0.1 *M* aqueous potassium acetate–acetic acid buffer, pH 4.6, a time-dependent absorbance change at 268 nm with a pseudo-first-order rate constant of approximately 5×10^{-2} sec^{-1} is observed (curve A, Figure 1). This result is most easily accounted for by the establishment of an equilibrium between the unhydrated and hydrated forms of the aldehyde. If an estimate is made for the absorbance of the hydrate at 268 nm, based on the absorbance of the corresponding bisulfite addition product, the magnitude of the observed absorbance change corresponds to 17 ± 1% hydration of the aldehyde at equilibrium.

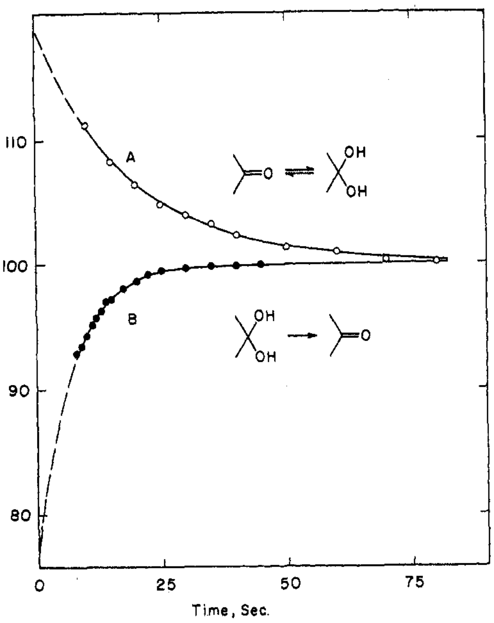
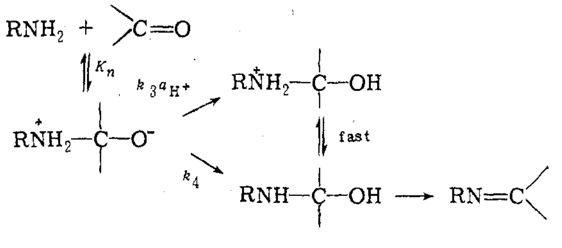


Figure 1. Time-dependent absorbance changes observed upon addition of *p*-nitrobenzaldehyde in acetonitrile solution to 0.1 *M* aqueous acetic acid–potassium acetate buffer, pH 4.6 (curve A), and *p*-nitrobenzaldehyde in aqueous solution to 0.5 *M* aqueous semicarbazide buffer, pH 2.8 (curve B). The spectral changes of curves A and B were followed at 268 and 320 nm, respectively, and corresponded to absolute absorbance changes of 0.080 (curve A) and 0.38 (curve B) for a total concentration of aldehyde in the reaction mixtures of 10^{-4} *M*. The broken portions of the curves represent extrapolated values determined from semilogarithmic plots of $(A_{obsd} - A_{final})$ or $(A_{final} - A_{obsd})$ against time.

(2) Addition of an *aqueous* solution of *p*-nitrobenzaldehyde to semicarbazide buffer, 88% acid, pH 2.8, causes an immediate burst of absorbance at 320 nm, followed by a measurably slow increase in absorbance to a final stable value (curve B, Figure 1). Under these conditions, the rate-determining step for semicarbazone formation is the proton transfer step, k_3 and k_4, in the formation of the cationic or neutral tetrahedral intermediate (eq 2),[5] and hence pre-



(2)

equilibrium accumulation of this intermediate is not responsible for the observed biphasic kinetics. The second phase that is observed in the reaction between *p*-nitrobenzaldehyde and 0.5 *M* (total) semicarbazide at pH 2.8 has a pseudo-first-order rate constant of 0.15 sec^{-1}, approximately 15 times slower than the pseudo-first-order rate constant, $K_n(k_3a_{H^+}+k_4)$ $[H_2NC(O)NHNH_2]$, of 2.3 sec^{-1} for buffer-independent semicarbazone formation under these conditions calculated from published rate constants.[5] The second phase of the reaction is less than first order in semicarbazide, as indicated by the fact that the pseudo-first-order rate constants for this process in the presence of