$\delta(CDCl_3)$ + 76.9 ppm]. The Δ_{Eu} values are $\Delta\delta$ values obtained by extrapolation to 1:1 molar ratio of ketone to $Eu(DPM)_3$ agent.

Registry No.—**1a**, 126-07-8; **1b**, 469-49-8; **2a**, 469-52-3; **2b**, 55658-69-0; **3**, 3573-90-8.

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Benzonorbornene-*endo*-2-carboxylic Acid and Its Methyl Ester[1]

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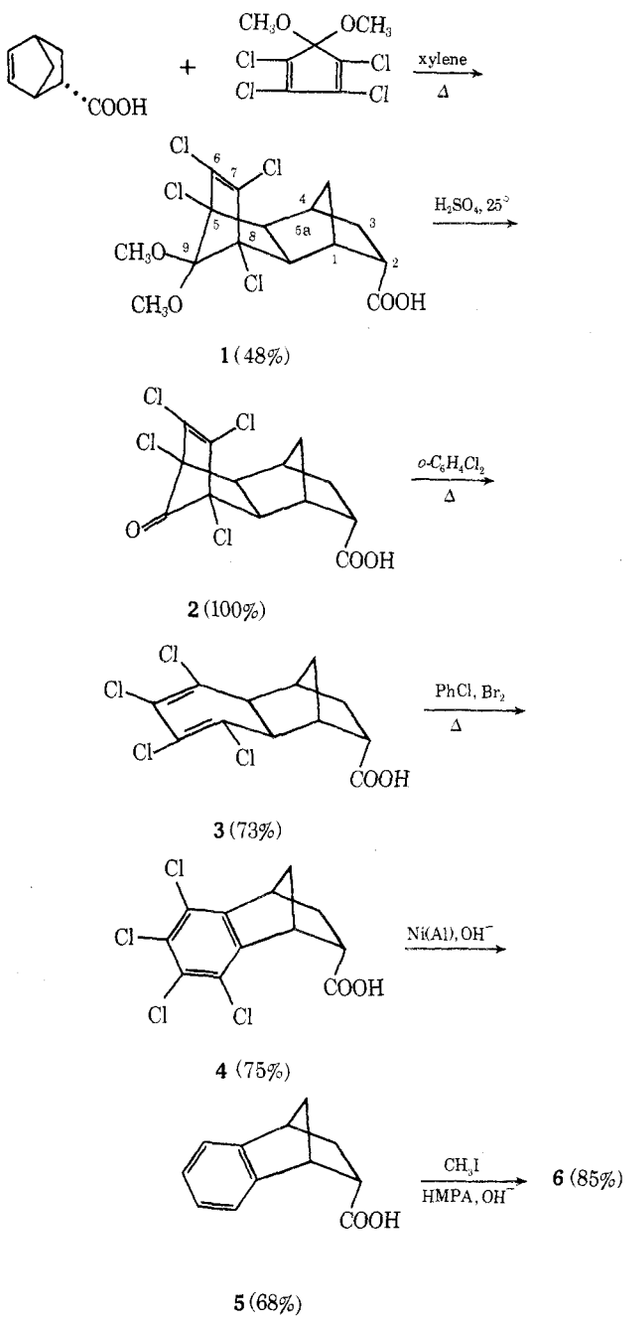
A need to confirm the structure of methyl benzonorbornene-*endo*-2-carboxylate (**6**) isolated in another study[2] led to the synthesis given in Scheme I. The sequence mirrors that used[3] to prepare the 1-carboxylic acid analog of **5** and requires no further discussion. However, the present use of the sequence involved an epimerizable acid function, in contrast to that earlier. The clean retention of configuration observed in **5** and **6**, with no trace of their exo epimers (both known[4]), shows that the sequence could have value as a general synthesis of ac-substituted benzonorbornenes of known stereochemistry, where ac = alicyclic in contrast to ar = aromatic.

Acid **5** was apparently unreported previous to our studies. However, two processes potentially capable of its synthesis have been reported. In the first, an ethyl ester possibly related to **6** was reported by Alder and Fremery,[5] but we have been unable to obtain **6** by their method (adduction of isoindene in situ with an acrylic ester). In the second, carbonation of the Grignard reagent obtained from *exo*-2-bromobenzonorbornene yielded only the exo 2 acid.[4]

Experimental Section

Melting points were taken on a calibrated Fisher-Johns block. Infrared spectra (ir) were determined on 1% KBr disks using a Perkin-Elmer Model 700 instrument. Only prominent or structurally significant absorptions are given (in microns). Nuclear magnetic resonance spectra (NMR) were taken in Me_2SO-d_6 solvent on a Varian A-60A spectrometer. Values are given in parts per million (δ) downfield from internal Me_4Si. Integration of signals agreed with the structural assignments. Mass spectra were taken on a Varian EM-600 instrument at 70 eV. Microanalyses were performed by the Micro-Tech Laboratories, Skokie, Ill.

Scheme I



5,6,7,8-Tetrachloro-9,9-dimethoxy-1,4:5,8-dimethano-1,2,3,4,5,5a,8,8a-octahydronaphthalene-*endo*-2-carboxylic Acid (1). A mixture of 5,5-dimethoxytetrachlorocyclopentadiene[6] (80.8 g, 0.306 mol) and norbornene-*endo*-2-carboxylic acid[7] (38.6 g, 0.263 mol) was refluxed in commercial xylene (150 ml) for 30 hr. Hexane (50 ml) was added and the solution was allowed to stand overnight. The precipitated material was collected and combined with some further material obtained by another treatment with hexane (100 ml): 53.5 g, 47.7%; mp 175–180°; ir 3.00–4.50, 5.88 (COOH), 6.24, 7.04, 7.69, 8.00, 8.40, 8.87, 9.52, 9.92, 10.38, 11.06, 13.15 μm; the compound was not soluble enough in the usual solvents to take a meaningful NMR spectrum. The analytical sample was obtained by recrystallization from xylene, mp 214–215°.

Anal. Calcd for $C_{15}H_{16}O_4Cl_4$: C, 44.80; H, 4.01. Found: C, 44.60; H, 4.01.

5,6,7,8-Tetrachloro-1,4-methano-1,2,3,4,5,5a,8,8a-octahydronaphthalene-*endo*-2-carboxylic Acid (3). Crude acid **1** (53.4 g, 0.133 mol) was added to concentrated sulfuric acid (250 ml) and stirred at 25° for 2 hr. The mixture then was poured over ice (625 g, the ratio of ice to sulfuric acid is critical, otherwise an oil results), stirred briefly, and filtered immediately. The solid so collected was crude keto acid **2** (47.3 g, quantitative yield) which was

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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Fluorinated Hydroquinones

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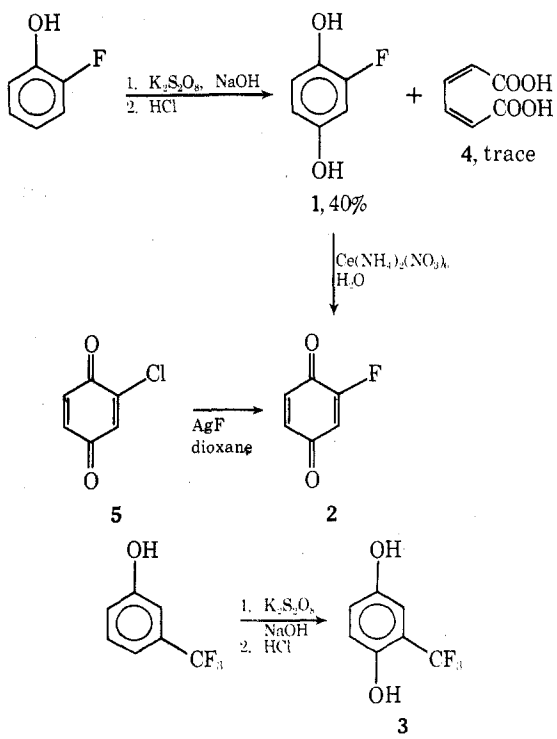
The fluorinated hydroquinones and benzoquinones possess interesting biological[1-3] and chemical[4-9] properties. Although some properties[2,3] of fluorohydroquinone (**1**) have been described, its preparation and spectroscopic characterization have not been detailed. A multistep preparation of fluorobenzoquinone (**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