4-Phenyl-4a,5,8,8a-tetrahydro-5,8-methano-1,2-naphthoquinone (2c).—To a chilled, stirred solution of 7.2 g. of iodic acid in 280 ml. of water was added, dropwise, a solution of 18.6 g. (0.1 mole) of 4-phenylcatechol in 280 ml. of acetone. The addition was complete in 1 hr. The brown precipitate which formed was collected by filtration and washed with 50% acetone and water (two 100-ml. portions). The material was air dried to give 18–20 g. of a brown solid, m.p. 104–105° dec., which was identified as 4-phenyl-*o*-quinone through its infrared spectrum. This material was converted to its diene adduct in the following manner. To a suspension of the above 4-phenyl-*o*-quinone in 400 ml. of petroleum ether (b.p. 30–60°) was added 13.2 g. of freshly prepared cyclopentadiene. To this suspension, 100 ml. of anhydrous ether was added and the mixture was stirred for 48 hr. The yellow precipitate which had formed during this time was collected, washed several times with petroleum ether, and air dried to give 21.5 g. (84.0%), m.p. 121–123°.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6. Found: C, 81.8; H, 5.7.

The infrared spectrum of this compound was consistent with the proposed structure, having carbonyl bands at 1660 and 1730 cm.$^{-1}$ and no hydroxyl absorption. The n.m.r. spectrum run in deuteriochloroform was also consistent with the proposed structure, showing two methylene protons at τ 8.38, two ring-junction protons at 5.98 and 6.90, two bridgehead protons at 6.52, two vinyl protons at 3.96, one α-ketovinyl proton at 3.36, and five aromatic protons at 2.44.

4-Phenyl-5,8-dihydro-5,8-methano-1,2-naphthohydroquinone Diacetate (3).—A mixture of 18.0 g. of **2c**, 10 ml. of anhydrous pyridine, and 350 ml. of acetic anhydride was heated on a steam bath for 2 hr. and then poured into 1000 ml. of ice–water. Continued stirring and trituration caused the gummy oil to solidify. This material was separated and recrystallized several times from ethanol to give a white crystalline material, m.p. 102–118°, yield 15.0 g.

Anal. Calcd. for $C_{21}H_{18}O_4$: C, 75.4; H, 5.4. Found: C, 75.1; H, 5.6.

Two samples were recrystallized using Darco G-60. One sample, with ethanol, gave short needles, m.p. 100–120°, and the other sample, with cyclohexane, gave square prisms, m.p. 101–120°. The filtrate from the cyclohexane recrystallization was condensed and crystallized from ether as long prisms, m.p. 101–121°.

A sample was dried at 65° (0.15 mm.) for 3 hr., m.p. 101–126°.

The preceding samples were combined and melted. Cooling for as long as 3 days did not cause crystallization, even after seeding. The sample crystallized from an ethanol solution, m.p. 101–121°, and had the same infrared spectrum as the initial material.

4-Phenyl-5,8-dihydro-5,8-methano-1,2-naphthohydroquinone.—The preceding diacetate (3.93 g.) was mixed with 100 ml. of methanol containing 1 drop of concentrated sulfuric acid. After the solution had been stirred under reflux for 18 hr., the methanol and methyl acetate were removed on a rotary evaporator at 50°. The resulting oil was taken up in ether and washed twice with water. Evaporation of the ether gave a white solid, 2.90 g., m.p. 136–138°. Recrystallization from benzene gave white needles, 1.91 g., m.p. 140–141°, with sintering at 137°.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6. Found: C, 81.5; H, 6.0.

The infrared spectrum showed no carbonyl band but a strong hydroxyl absorption at 3300 cm.$^{-1}$. The n.m.r. spectrum run in deuteriochloroform showed two methylene bridge protons at τ 7.83, two bridgehead protons at 5.93, two vinyl protons at 3.14, one aromatic proton at 3.50, two hydroxyl protons at 4.74, and the phenyl protons at 2.63.

This product (1.25 g.) was added to a mixture of 3.06 g. of acetic anhydride and 10 ml. of pyridine. The solution was refluxed for 3 hr. and allowed to stand at room temperature for 18 hr. The solution was poured into 150 ml. of ice–water and the resulting solid was filtered and washed with water. The product was mixed with ice-cold 0.5 *N* hydrochloric acid, then filtered, and washed with water. Recrystallization from ethanol gave 0.95 g., melting at 99.5–116.5°. An infrared spectrum was identical with that of the compound (**3**) prepared from the acetylation of the enedione **2**.

Spirodioxolanonarenones. II.[1] Synthesis of a Halogenated 1,4-Dioxaspiro[4,5]deca-7,9-diene-2,6-dione

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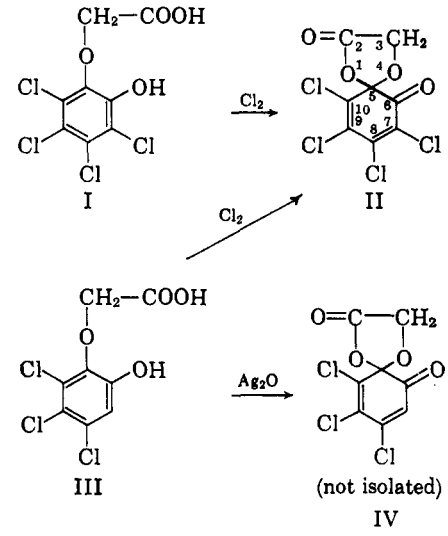
In a previous paper[1] the synthesis of spirodioxolanon-*p*-arenones[2] by oxidation of the corresponding *p*-hydroxyphenoxyacetic acids was reported. Postulating the same reaction conditions for *para* and *ortho* compounds, the oxidation of several *o*-hydroxyphenoxyacetic acids was examined. Since we had found that the reaction occurred readily on compounds bearing electron-attracting substituents,[1] halogenated derivatives were chosen as starting materials for the *ortho* series also.

2-Hydroxy-3,4,5,6-tetrachlorophenoxyacetic acid[3] (I) was oxidized in dry ether with chlorine to give a product with the composition $C_8H_2Cl_4O_4$. The infrared spectrum (two carbonyl bands at 1825 and 1708 cm.$^{-1}$), the n.m.r. spectrum (one peak at $\delta = 4.73$ p.p.m.), and the ultraviolet spectrum (absorption band at 368 mμ) led to the identification as 7,8,9,10-tetrachloro-1,4-dioxaspiro[4,5]deca-7,9-diene-2,6-dione (II). The oxidation of I with bromine failed to produce the spiroarenone compound, showing that the *o*-hydroxyphenoxyacetic acids have a higher oxidation potential than the corresponding *para* compounds.



2-Hydroxy-4,5,6-trichlorophenoxyacetic acid (III), obtained from 2-methoxy-4,5,6-trichlorophenoxyacetic acid, was also oxidized to II with chlorine due to facile halogenation at position 3. The oxidation of III with silver oxide in nonhydroxylic solvents such as benzene gave a crude product, probably the expected 8,9,10-

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(2) We adopted the name arenones as suggested by L. F. Fieser and M. Fieser ("Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 875) for dienones derivable or convertible into aryl hydroxy compounds.

(3) J. Myska and V. Ettel, *Collection Chem. Commun.*, **26**, 895 (1961); *Chem. Abstr.*, **55**, 16459 (1961).

trichloro-1,4-dioxaspiro[4,5]deca-7,9-diene-2,6-dione (IV) (infrared bands at 1820 and 1680 cm.$^{-1}$) which could not be purified. Treatment of III with other oxidizing agents such as hydrogen peroxide, ammonium persulfate, and ceric sulfate, did not produce the expected arenone.

Oxidation of 2-hydroxy-3,5-dibromophenoxyacetic acid with silver oxide in benzene likewise gave a crude product with infrared bands at 1825 and 1700 cm.$^{-1}$, characteristic of the *o*-arenone. As in the case of IV, a pure product could not be obtained because of the instability of the incompletely halogenated arenone system.[1]

Experimental

Melting points are uncorrected. The ultraviolet spectra were recorded on a Beckman Model DK-2 spectrometer. The infrared spectra were taken in Nujol mull with a Perkin-Elmer Model 125 spectrometer. The n.m.r. spectra were obtained on a Varian A-60 instrument in deuterioacetone, using tetramethylsilane as internal standard; the chemical shifts are expressed in δ-units.

7,8,9,10-Tetrachloro-1,4-dioxaspiro[4,5]deca-7,9-diene-2,6-dione (II).—In a solution of 5 g. of 2-hydroxy-3,4,5,6-tetrachlorophenoxyacetic acid (I)[3] in 250 ml. of dry ethyl ether CaO (12.5 g.) was suspended and chlorine was bubbled with stirring during 10 min. The solution was stirred for 1 hr., then filtered, and evaporated to dryness. Four grams of residue was obtained, which, crystallized from butanol, yielded pale yellow needles: m.p. 105–107°, infrared (Nujol) 1825 (νC-2=O) and 1708 cm.$^{-1}$ (νC-6=O), δ (CD_3COCD_3) 4.73 (methylene), and $\lambda_{max}^{CCl_4}$ 368 mμ (ϵ 4300).

Anal. Calcd. for $C_8H_2Cl_4O_4$: C, 31.61; H, 0.66; Cl, 46.67. Found: C, 31.70; H, 0.84; Cl, 46.12.

2-Methoxy-4,5,6-trichlorophenoxyacetic Acid.—A solution of 50 g. of 2-methoxy-4,5,6-trichlorophenol,[4] 31 g. of chloroacetic acid, and 22 g. of NaOH in 1000 ml. of water was refluxed for 35 hr. The warm solution was acidified and, after cooling, the precipitate was collected and then dissolved in 0.5 *N* NaOH. The solution was acidified to pH 6.0 and the unreacted phenol was filtered off. The solution was then acidified to pH 1 and the precipitate was collected and crystallized from ethanol–water (1:1) and then from benzene, yielding 15 g. of white needles: m.p. 147°; δ (CD_3COCD_3) 8.25 (singlet, 1H, carboxylic proton), 7.24 (singlet, 1H, aromatic proton), 4.73 (singlet, 2H, methylene), and 3.95 (singlet, 3H, methoxyl).

Anal. Calcd. for $C_9H_7Cl_3O_4$: C, 37.86; H, 2.47; Cl, 37.26. Found: C, 37.72; H, 2.60; Cl, 37.43.

2-Hydroxy-4,5,6-trichlorophenoxyacetic Acid (III).—Ten grams of the above methoxy acid was refluxed in 250 ml. of 48% HBr for 5 hr. On cooling a crop of white needles was obtained, which, crystallized from water and then from toluene, yielded 4 g. of product: m.p. 140–141°; δ (CD_3COCD_3) 8.80 (singlet, 2H, carboxylic and phenolic protons), 7.10 (singlet, 1H, aromatic proton), and 4.85 (singlet, 2H, methylene).

Anal. Calcd. for $C_8H_5Cl_3O_4$: C, 35.39; H, 1.86; Cl, 39.18. Found: C, 35.27; H, 2.00; Cl, 39.60.

2-Hydroxy-3,5-dibromophenoxyacetic Acid.—To a stirred solution of 5 g. of 2-hydroxyphenoxyacetic acid in 50 ml. of dioxane at 60° was gradually added 8 ml. of pyridine together with a solution of 3.2 g. of bromine in 200 ml. of dioxane. The reaction was stirred for 1 hr. after all of the bromine was added. Pyridine hydrobromide was filtered off; the solution was evaporated under vacuum to 50 ml. and then diluted to 500 ml. with 2 *N* HCl to give colorless crystals which were recrystallized from benzene: m.p. 157–158°; δ (CD_3COCD_3) 9.10 (singlet, 2H, carboxylic and phenolic protons), 7.32 (doublet, J = 2.5 c.p.s., 1H) and 7.18 (doublet, J = 2.5 c.p.s., 1H) (two aromatic protons in *meta* position), and 4.85 (singlet, 2H, methylene).

Anal. Calcd. for $C_8H_6Br_2O_4$: C, 29.47; H, 1.85; Br, 49.05. Found: C, 29.63; H, 1.93; Br, 49.39.

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A Facile Synthesis of 3β-Acetoxy-20-keto-5,14,16-pregnatriene[1]

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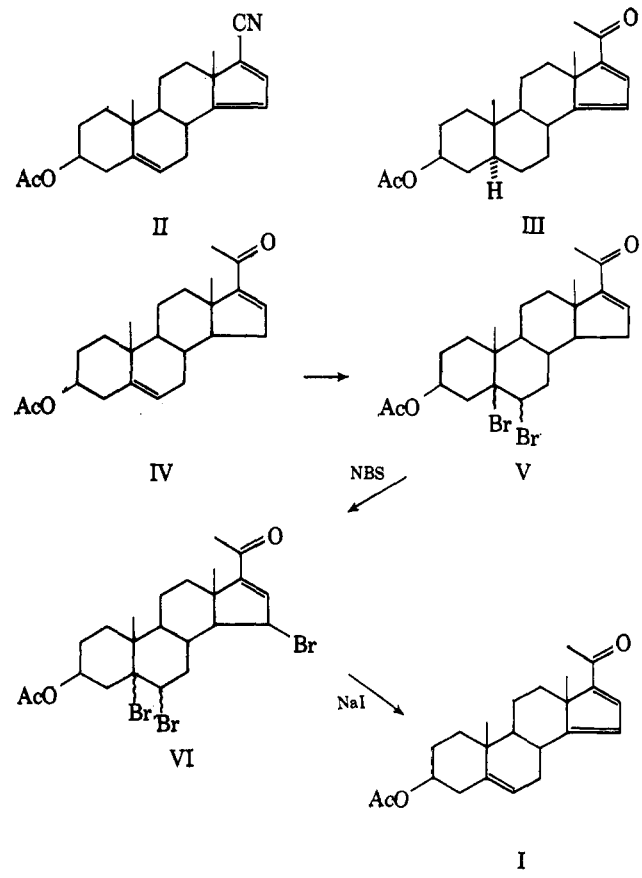
In connection with our projected synthesis of ring-D-bridged analogs of the steroid hormones,[3] it became necessary to secure a supply of 5,14,16-pregnatrien-3β-ol-20-one acetate (I). The only synthesis of I which we have been able to find in the literature involves Grignard addition to 3β-acetoxy-17-cyano-5,-14,16-androstatriene (II).[4] Since, in our previous work,[3] we found the synthesis of II[4] to be difficult and overly long, we decided to seek a more facile path to I.

The synthesis of 3β-acetoxy-20-keto-5α-pregna-14,-16-diene (III) has been reported by a path involving conversion of 3β-acetoxy-5α-pregnan-20-one to its 16-dehydro derivative, followed by bromination at C-15 and subsequent dehydrobromination.[5] Because the separation of III from the intermediate 16-dehydro



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