2.57 g. (0.11 g.-atom) of sodium. Stirring was then initiated. The system was swept with dry nitrogen throughout the experiment. Almost immediately after adding the sodium the solution began to boil and it became dark. After several minutes boiling stopped; at this point the sodium had a very shiny luster. The mixture was stirred for a total of 0.5 hr. at ice temperature and then about 50 ml. of water was carefully added. The petroleum ether was expelled by evacuation and the residual aqueous solution[14] was steam distilled. The distillate was extracted with ether; the extracts were dried over anhydrous potassium carbonate and distilled. There was obtained 4.00 g. (62% yield) of levorotatory 2-octanol, b.p. 45° (1 mm.), $n^{20}\text{D}$ 1.4260, $\alpha^{25}\text{D}$ −4.81°.

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.92. Found: C, 73.90; H, 13.86.

Cleavage of (−)-α-Phenylethyl Nitrate by Potassium.—In a 300-ml. flask (oven dried and swept with dry nitrogen while cooling) was placed 50 ml. of petroleum ether[13] (b.p. 90–100°), 10 g. of sand (washed with hydrochloric acid and water and ignited just before using), potassium (8.75 g., 0.224 g.-atom), and levorotatory α-phenylethyl nitrate (12.5 g., 0.075 mole), b.p. 58° (1 mm.), $n^{20}\text{D}$ 1.5089, $\alpha^{27}\text{D}$ −1.80°. Stirring was begun and the system was flushed with nitrogen from time to time. About 5 min. after the addition of the nitrate ester the potassium was covered with a brown coating. Up to this point the reaction had been run at room temperature. The flask was now placed in ice for *ca.* 2 hr. and then it was maintained at room temperature for *ca.* 15 hr. The mixture was then cooled to 0°, cold methanol (*ca.* 50 ml.) was added slowly, and then the product was added to *ca.* 200 ml. of water and steam distilled. The distillate was saturated with sodium chloride and extracted with ethyl ether. After drying, the ether solution was distilled. There was obtained 2.30 g. (25% yield) of levorotatory α-phenylethyl alcohol, b.p. 53° (1 mm.), $n^{20}\text{D}$ 1.5271, $\alpha^{26}\text{D}$ −1.04°.

Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.75; H, 8.25.

Reaction of Ethylmagnesium Bromide with (−)-α-Phenylethyl Nitrate.—The Grignard reagent prepared from 70 g. (0.64 mole) of ethyl bromide and 15 g. (0.62 g.-atom) of magnesium was cooled to −5°. To it 20 g. (0.12 mole) of levorotatory α-phenylethyl nitrate ($\alpha^{27}\text{D}$ −3.28°, $n^{20}\text{D}$ 1.5091), diluted with 100 ml. of ethyl ether, was added dropwise while stirring and cooling at −5°. The reaction was immediate and vigorous. After addition of the nitrate was complete, the reaction mixture was allowed to warm to room temperature and agitated for 24 hr. It was then acidified with 5% sulfuric acid while keeping the temperature below 5°. The ether layer was washed with sodium bicarbonate and with water before drying over magnesium sulfate. Fractionation of the product through a short column gave 9.8 g. (68% yield) of pure levorotatory α-phenylethyl alcohol ($n^{20}\text{D}$ 1.5274, $\alpha^{27}\text{D}$ −2.90°).

Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.46; H, 8.43.

The infrared spectrum of this material was superimposable on that of authentic α-phenylethyl alcohol.

Reduction of (−)-α-Phenylethyl Nitrate with Ammonium Polysulfide.—This reaction was carried out according to the procedure of Merrow and Van Dolah[4] except that it was only allowed to proceed for 1 day at room temperature. From 10.7 g. (0.064 mole) of levorotatory α-phenylethyl nitrate, b.p. 58° (1 mm.), $n^{20}\text{D}$ 1.5089, $\alpha^{25}\text{D}$ −6.05°, there was obtained 0.85 g. (11% yield) of levorotatory α-phenylethyl alcohol, b.p. 57° (1 mm.), $n^{20}\text{D}$ 1.5268–1.5269, $\alpha^{27}\text{D}$ −3.59°.

Reaction of (−)-α-Phenylethyl Nitrate with Lithium Chloride.—A mixture of 8 g. of levoratory α-phenylethyl nitrate ($\alpha^{27}\text{D}$ −3.28°), 100 ml. of acetone which had been dried over Drierite and distilled directly into the reaction flask, and excess lithium chloride (10 g.), was refluxed for 60 hr. The reaction product was poured into a mixture of petroleum ether (b.p. 65–67°) and ice water, and the organic layer was then washed with water, dried, and fractionally distilled. The 3.65 g. of product had $\alpha^{27}\text{D}$ +4.35°, $n^{20}\text{D}$ 1.5265–1.5269. This α-phenylethyl chloride was, however, contaminated by a small amount of α-phenylethyl nitrate as shown by the infrared spectrum. Consequently, 2.55 g. of this chloride was treated with lithium chloride as before for an additional 72 hr. On working up the reaction mixture 2.35 g. of dextorotatory α-phenylethyl chloride ($\alpha^{27}\text{D}$ +3.17°, $n^{20}\text{D}$ 1.5267–1.5269) was isolated. This had an infrared spectrum superimposable on that of authentic α-phenylethyl chloride; no nitrate ester band was present.

Anal. Calcd. for C_8H_9Cl: C, 68.33; H, 6.46; Cl, 25.25. Found: C, 68.12; H, 6.21; Cl, 25.06.

Optical Stability of α-Phenylethyl Chloride in Presence of Chloride Ion.—α-Phenylethyl chloride (0.5 g., $\alpha^{25}\text{D}$ +33.4°) was added to a slurry of excess lithium chloride in 5 ml. of acetone and refluxed for 20 hr. The recovered α-phenylethyl chloride had $\alpha^{27}\text{D}$ +30.5°.

The Reaction of (+)-α-Phenylethyl Nitrate with Sodium Methoxide in Methanol.—At 20° a 0.4786 *M* solution of α-phenylethyl nitrate in methanol containing sodium methoxide (1.163 *M*) gave a second-order rate constant ($k = 1.86 \pm 0.02 \times 10^{-2}$ l. mole^{-1} hr.$^{-1}$) over the first 65% of the reaction.

Eight grams (0.047 mole) of dextrorotatory α-phenylethyl nitrate ($\alpha^{26}\text{D}$ +1.63°, $n^{20}\text{D}$ 1.5089) was added to solution of sodium (2.35 g., 0.102 g.-atom) in 50 ml. of methanol. The resulting clear solution was stirred at room temperature under dry nitrogen for 12 hr. after which stirring was discontinued. After a total of 132 hr. at room temperature, the white solid which had formed was isolated by filtration and washed with ether. This solid was insoluble in common organic solvents but dissolved in water; it decomposed upon heating in a Bunsen flame, but did not burn; it gave a brown ring test with ferrous sulfate and sulfuric acid. When a sample was added to aniline in cold hydrochloric acid and this solution in turn was added to a basic solution of β-naphthol, no red precipitate was formed. The solid weighed 3.08 g. (77% yield calcd. as $NaNO_3$). The methanolic filtrate was poured into water and extracted with ether, and the extracts were washed with water and dried over magnesium sulfate. Distillation through a small column gave 3.59 g. (56% yield) of levorotatory methyl α-phenylethyl ether, b.p. 76° (30 mm.), $n^{20}\text{D}$ 1.4915–1.4917, $\alpha^{26}\text{D}$ −3.79°.

Anal. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.29; H, 9.04.

Reduction with Lithium Aluminum Hydride. A. 2-Octyl Nitrate.—Levoratory 2-octyl nitrate ($\alpha^{28}\text{D}$ −2.71°, $n^{20}\text{D}$ 1.4249) was reduced as described by Soffer, Parrotta, and Di Domenico[5] except that the reaction was first conducted at 0° for 57 hr. and then at 25° for 27 hr. An 80% yield of 2-octanol, $\alpha^{25}\text{D}$ −1.10°, b.p. 55° (3 mm.), $n^{20}\text{D}$ 1.4260, was obtained.

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.93. Found: C, 73.76; H, 13.65.

B. α-Phenylethyl Nitrate.—This reduction was conducted at 0° for 200 hr. during which time relatively little gas was evolved. The product was a mixture from which no pure compound was isolated but which appeared to contain much ethyl benzene.

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[14] Prior to steam distillation a small portion of the aqueous solution was added to aniline in cold hydrochloric acid. The resulting solution gave a red precipitate with sodium β-napthoxide.

The Preparation of Diene Adducts of *o*-Quinones

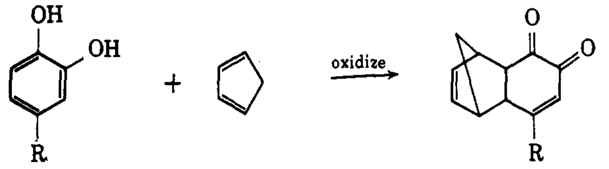
F. J. EVANS, H. S. WILGUS, III, AND J. W. GATES, JR.

Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650

Received July 13, 1964

The reaction of dienes with *p*-quinones and the rearrangement of these adducts to hydroquinone derivatives have been known for many years.[1] Very little has been reported concerning the diene adducts of *o*-quinones,[2] perhaps because of the known instability of the *o*-quinones. It appeared of interest to prepare several cyclopentadiene adducts of *o*-quinones.

Since the simple *o*-quinones are not noted for their stability,[3] two of the three described in this Note were prepared by oxidative procedures in the presence of excess diene (cyclopentadiene) and were thus trapped and isolated as the desired adducts. The three quinones and their adducts are shown below.

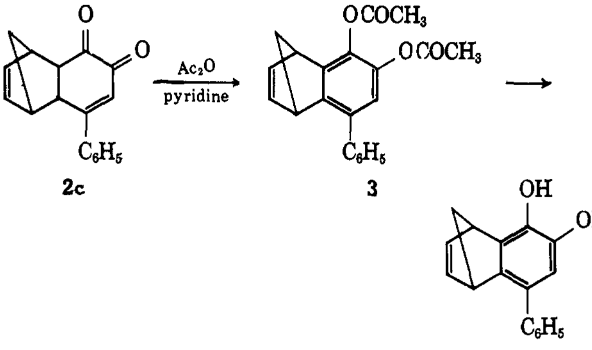


1 2

a, R = H
b, R = CH_3
c, R = C_6H_5

Unfortunately, the adducts **2a–c** are no more stable than the parent *o*-quinones, possibly because of a tendency toward rearrangement or dissociation into the original components, with subsequent decomposition of the *o*-quinone.

It has been reported that the diene adducts of *p*-benzoquinone, in many cases, will rearrange to hydroquinones with acid, heat, or alkali. The rearrangement of the cyclopentadiene *p*-benzoquinone adducts has recently been reported.[4,5] The rearrangement was carried out in acetic anhydride in the presence of a base catalyst (*e.g.*, pyridine, triethylamine) and the hydroquinones were isolated as the stable diacetates. One of the *o*-quinone adducts, **2c**, was treated in a similar manner.



2c 3 4

From this reaction, 4-phenyl-5,8-dihydro-5,8-methano-1,2-naphthohydroquinone diacetate (**3**) was obtained as a white crystalline material. This compound, however, melted over a wide range (102–118°). Recrystallization from ethanol, cyclohexane, and ether gave different crystalline forms but an unimproved melting point. The melted samples could not be induced to crystallize by standing or seeding but gave the same crystalline product when redissolved in ethanol. The infrared spectrum of this solid showed a carbonyl group at 1765 cm.$^{-1}$ but no hydroxyl group. Vapor phase chromatography (v.p.c.) on a 2-ft. Apiezon column at 280° gave one sharp peak having a retention time of 7 min.; v.p.c. on a 4-ft. silicone oil column at 250° gave a single peak having a retention time of 6 min. A mass spectrum was consistent with the proposed structure in that the molecular weight was correct and the fragmentation suggested two acetoxy groups. A sample of material was chromatographed on the silicone oil column and the peak fraction was collected. A mass spectrum of this sample was the same as that of the original sample. An n.m.r. spectrum in deuteriochloroform showed five aromatic protons at τ 2.62, one aromatic proton at 3.20, two vinyl protons at 3.14, the two bridgehead protons at 6.02, and the two acetate methyl groups at 7.72 and 7.78, with the two methylene protons falling under the peak at 7.78. An n.m.r. spectrum in pyridine confirmed this last observation, showing the two methyl groups at τ 7.68 and 7.76 and the two methylene protons at 7.88.

Hydrolysis of the diacetate **3** using methanol and a catalytic amount of sulfuric acid gave 4-phenyl-5,-8-dihydro-5,8-methano-1,2-naphthohydroquinone (**4**). This product was obtained in good yield and melted sharply. Combustion analysis and the infrared and n.m.r. spectra were all consistent with the proposed structure. A sample of this product (**4**) was reacetylated to give the diacetate **3** having the same broad melting point. The wide melting range for compound **3** remains unexplained.

Experimental

4a,5,8,8a-Tetrahydro-5-methano-1,2-naphthoquinone (2a).—To a stirred, chilled solution of 5.5 g. (0.05 mole) of pyrocatechol and 3.3 g. of cyclopentadiene in 200 ml. of 80% ethanol was added a solution of 3.6 g. of iodic acid in 100 ml. of 80% ethanol. The addition took place over the course of 0.5 hr. The resulting red solution was stirred vigorously for 1 hr. and stored at 0° for 48 hr. The solution was then partially decolorized with Norit and concentrated on a rotary evaporator. The residue was extracted with benzene. The benzene extracts were washed with water, dried over anhydrous $MgSO_4$, and again decolorized with Norit. The solvent was removed under reduced pressure and the residue was crystallized with ligroin (b.p. 60–90°) and isopropyl alcohol. The yellow solid was recrystallized from isopropyl alcohol and ligroin to give 3.4 g. (39.1%), m.p. 89–91°. The identity of this material was shown by comparison of its infrared spectrum with the spectra of the two examples described in the next paragraphs.

4-Methyl-4a,5,8,8a-tetrahydro-5,8-methano-1,2-naphthoquinone (2b).—To a solution of 6.2 g. (0.05 mole) of 4-methylcatechol in 250 ml. of anhydrous ether were added 35.0 g. of freshly prepared Ag_2O and 35.0 g. of Na_2SO_4. The mixture was stirred under nitrogen for 1 hr. and then filtered through Celite. To the red filtrate, 5.0 g. (0.05 mole) of cyclopentadiene was added and the solution was stirred for an additional 24 hr. The yellow solution was taken to dryness on a rotary evaporator and the red residue was crystallized, with some difficulty, from ligroin and isopropyl alcohol. The yellow crystalline material was recrystallized several times from petroleum ether (b.p. 66–75°) and isopropyl alcohol to give 4.5 g. (47.9%), m.p. 79–80°.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.6; H, 6.4. Found: C, 76.8; H, 6.7.

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(1) O. Diels and K. Alder, *Ber.*, **62**, 2337 (1929).

(2) L. W. Butz, *Org. Reactions*, **5**, 136 (1949).

(3) J. Cason, *ibid.*, **4**, 305 (1948).

(4) J. Meinwald and G. A. Wiley, *J. Am. Chem. Soc.*, **80**, 3667 (1958).

(5) R. F. Porter, W. W. Rees, E. Frauenglass, H. S. Wilgus, III, G. H. Nawn, P. P. Chiesa, and J. W. Gates, Jr., *J. Org. Chem.*, **29**, 588 (1964).

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

Gian Gualberto Gallo, Carmine Renato Pasqualucci,
and Alberto Diena

Research Laboratories of Lepetit S.p.A., Milan, Italy

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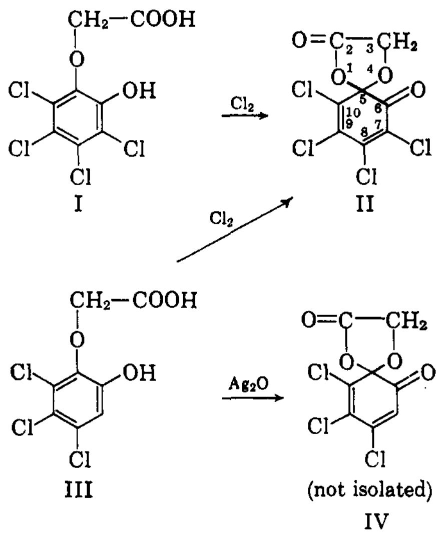
In a previous paper[1] the synthesis of spirodioxolanon-*p*-arenones[2] by oxidation of the corresponding *p*-hydroxyphenoxyacetic acids was reported. Postulating the same reaction conditions for *para* and *ortho* compounds, the oxidation of several *o*-hydroxyphenoxyacetic acids was examined. Since 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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[1] Part I: G., G. Gallo, C. R. Pasqualucci, and P. Sensi, *Ann. chim.* (Rome), **52**, 902 (1962).

[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).