Electron-Transfer Polymers. XXVI. Synthesis of Oligomeric Hydroquinones and *p*-Benzoquinones

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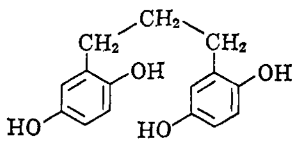
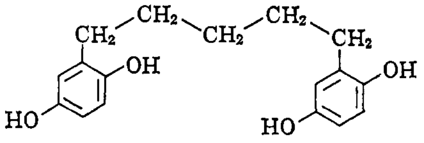
The syntheses of 1,3-bis(2,5-dihydroxyphenyl)propane, 1,5-bis(2,5-dihydroxyphenyl)pentane, and 1,3,5-tris-(2,5-dihydroxyphenyl)pentane are reported. The oxidation-reduction behavior of these substances and of hydroquinone and ethylhydroquinone reference compounds, in 90% aqueous acetic acid and 1% aqueous acetic acid, and the E_0 values, which for all the substituted hydroquinones fall within the range 0.637–0.640 v. in 1% acetic acid and 0.618–0.625 v. in 90% acetic acid (calculated to the hydrogen scale and pH 0.0), are reported and discussed. The ultraviolet and visible absorption spectra in 95% aqueous tetrahydrofuran for all these five substances in the hydroquinonyl state, as the dimethyl hydroquinonyl ethers, and in the benzoquinonyl (oxidized) state are reported and discussed. During oxidation the rings of the bis and tris compounds seem to react independently, unlike the behavior of the functional groups in sulfonated polyvinylhydroquinone. When oxidized in a highly aqueous solvent the 1,3-bis and the 1,3,5-tris compounds develop a red color, the intensity of which reaches a maximum at the midpoint. They thus behave in this respect like vinylhydroquinone homopolymers.

When the electron-transfer (oxidation–reduction) polymer, polyvinylhydroquinone, or the sulfonated homo polymer, is oxidatively titrated, the solution, initially colorless, undergoes a striking color development. With the first addition of oxidant a pink color appears. This increases in intensity to the midpoint of the titration, then shows more and more yellow until at the end point the clear yellow of polyvinyl-*p*-benzoquinone alone is present.[1–3] When the oxidative potentiometric titration curve for polymer that has been sulfonated to make it water soluble is plotted on a per cent oxidized basis,[4] the curve is found to be unexpectedly flat, deviating considerably from the normal two-electron curve with its index potentials of 14 mv.[5] The potential at the midpoint is found to be substantially higher than that of sulfonated isopropylhydroquinone, a reference monomer that represents a segment of the polymer chain, and the approach to equilibrium upon each addition of titrant is exceptionally slow.[4] It was suspected that the color reflected intramolecular quinhydrone formation, but the sources of the other marked differences between oxidation–reduction polymer and monomer, referred to above, were obscure.

It was therefore decided to prepare oligomeric materials which resemble fragments of the polymer so as to see whether light could be shed through a study of these simpler species upon the behavior of polyvinylhydroquinone. Hunt and Lindsey have also used this approach in connection with their study of hydroquinone–formaldehyde polymers.[6] Whether such an approach is justified is difficult to state *a priori*. For example, it is known from protein studies[7] that the conformational properties of a polymer are not necessarily duplicated by oligomers. This paper reports the synthesis of 1,3-bis(2,5-dihydroxyphenyl)propane (I), 1,5-bis(2,5-dihydroxyphenyl)pentane (II), and 1,3,5-tris(2,5-dihydroxyphenyl)pentane (III), and the oxidation–reduction behaviors and absorption spectra of these compounds. Included also for comparison are the relevant properties of the monomeric substances hydroquinone and ethylhydroquinone.



I



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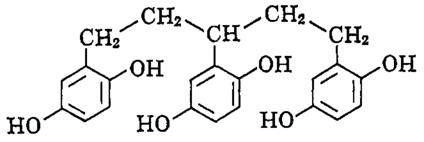

III

Spectra.—The ultraviolet and visible absorption spectra of the three oligomers and two reference compounds as their methyl ethers and in their fully oxidized and fully reduced states are reported in Table I. The solvent, 95% aqueous tetrahydrofuran, was chosen for solubility reasons.

Hunt and Lindsey,[6] in their discussion of the ultraviolet absorption spectra of several methylene-linked quinones, hydroquinones, and hydroquinone dimethyl ethers, came to the conclusion that interactions between neighboring π-electron systems are likely to be reflected in these spectra.[8] They suggested that interactions may arise as the result of the inductive or polarizing effects of neighboring groups or through electron delocalization between the rings and the adjoining methylene bridge owing to conjugative effects, especially hyperconjugation. Further possible ring–ring interactions could arise intramolecularly as a result of interspacial polarization effects or through hydrogen bonding.

In all of the oligomers in Table I the aromatic systems are separated by three or five saturated carbon atoms.

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(1) H. G. Cassidy and K. A. Kun, "Oxidation–Reduction Polymers," Interscience Publishers, Inc., New York, N. Y., 1965.

(2) H. Kamogawa, Y. C. Giza, and H. G. Cassidy, *J. Polymer Sci.*, **A2**, 4647 (1964).

(3) H. G. Cassidy, *J. Am. Chem. Soc.*, **71**, 402 (1949).

(4) I. D. Robinson, M. Fernandez-Refojo, and H. G. Cassidy, *J. Polymer Sci.*, **39**, 47 (1959).

(5) W. M. Clark, "Oxidation–Reduction Potentials of Organic Systems," Williams and Wilkens Co., Baltimore, Md., 1960.

(6) S. E. Hunt and A. S. Lindsey, *J. Chem. Soc.*, 4550 (1962).

(7) P. Arens and P. Doty, *Advan. Protein Chem.*, **16**, 401 (1961).

(8) E. A. Braude, *J. Chem. Soc.*, 1902 (1949).

TABLE I

ULTRAVIOLET AND VISIBLE ABSORPTION SPECTRA IN 95 VOL. % AQUEOUS TETRAHYDROFURAN

Compd.	λ_{max}, mμ	ϵ_{mol}
Hydroquinone	298	3,480
Hydroquinone dimethyl ether	226	10,000
	290	3,200
p-Benzoquinone	243	20,800
	435	18
Ethylhydroquinone	298	3,880
Ethylhydroquinone dimethyl ether	230	5,680
	292	3,210
Ethyl-*p*-benzoquinone	248	18,000
	315	800
	435	25
1,3-Bis(2,5-dihydroxyphenyl)propane	299	8,800
1,3-Bis(2,5-dimethoxyphenyl)propane	229	11,400
	292	7,700
1,3-Bis(*p*-benzoquinonyl)propane	248	41,300
	315	1,650
	444	58
1,5-Bis(2,5-dihydroxyphenyl)pentane	299	7,800
1,5-Bis(2,5-dimethoxyphenyl)pentane	232	9,000
	292	7,370
1,5-Bis(*p*-benzoquinonyl)pentane	249	31,400
	315	1,570
1,3,5-Tris(2,5-dihydroxyphenyl)pentane	299	11,520
1,3,5-Tris(2,5-dimethoxyphenyl)pentane	232	15,900
	292	11,600
1,3,5-Tris(*p*-benzoquinonyl)pentane	249	44,800
	315	2,770

Consequently, some of the above-mentioned modes of interaction can be of minimal importance only. Inductive effects extending over three and especially five carbon atoms are extremely weak and do not affect the spectra. Indeed, Hunt and Lindsey[6] found that when two aromatic rings were separated by an ethylene linkage, the absorption intensity of the isolated chromophores assumed an approximately additive value. Conjugative effects between the rings are also eliminated when the carbon bridge is extended beyond two members.

Interactions of the charge-transfer type are generally associated with the appearance of a new absorption band. Since no such new absorption bands are observed (Table I), any interaction of this type must contribute little to any other observable changes in the spectrum. Intramolecular hydrogen bonds can contribute effects only to the hydroquinonyl forms of the oligomers. Molecular models indicate that there are no serious steric hindrances in any of the compounds. Deviations from the additivity of absorption intensities, and changes in wave length as the complexity of the molecules is increased, must then originate primarily from transition mixing, or from dispersion-force interactions between neighboring chromophore groups.

The ultraviolet spectrum of *p*-dimethoxybenzene possesses two principal absorption maxima, at 226 and 290 mμ. These are considered to correspond to the 200- and 260-mμ bands of benzene.[9]

Ethylhydroquinone dimethyl ether was chosen as the model monomer for comparison of the additivity of absorption intensities and positions. Understandably, the intensity of the shorter wave length band of the 1,3-propylene-linked ether was twice that of the 230-mμ band of the model compound. In contrast, the corresponding bands of both 1,5-pentylene-linked compounds were less intense then expected on this basis. In all cases, the positions of the bands remained virtually unchanged in passing through the series. Similarly, the 292-mμ bands, although not shifting in position throughout the series, showed absorption intensities somewhat in excess of those predicted by summing the intensities of the relevant "fragments." The spectra of the hydroquinonyl forms of the oligomers were almost identical, in wave-length maximum and intensity, with that of ethylhydroquinone.

The electronic spectra of *p*-benzoquinone and its derivatives have been studied by Orgel,[10] who recognized that of the three main absorptions of quinone, at 410, 282, and 250 mμ, the first is $n \rightarrow \pi^*$, and the latter two probably $\pi \rightarrow \pi^*$ in character. In all three quinonyl oligomers, the $\pi \rightarrow \pi^*$ transitions have been assigned the nearly invariant wave lengths of 249 and 315 mμ. Monosubstitution on *p*-benzoquinone caused the $n \rightarrow \pi^*$ transition to become broad, diffuse, and of little analytical value in the present discussion. Comparison of the molar extinction coefficients of the quinonyl forms of the oligomers gives a distorted image of the actual intensities of the curves. Addition and comparison of molar extinction coefficients, to be accurate, require that the curves have nearly identical shapes. This condition was fulfilled in the cases of hydroquinones and their ethers. In situations in which curves shapes vary, integrated intensities should be compared. As the molecular weight and number of quinonyl groups per molecule were increased in the oxidized oligomers, the 249-mμ band decreased in height and became broader. Integration of the peak areas gave values in each case which were nearly equal to those expected by summing the integrated intensities of the relevant fragments. The greatest amount of deviation from the summed intensity was displayed by the 1,5-propylene-bridged oligomer, the 249-mμ band of which slightly exceeded the predicted value.

The ultraviolet absorption spectra suggest that there is very little interaction between the π-electron systems of the fully reduced and fully oxidized forms of the oligomers. Weak interaction of an unknown origin appears to affect the spectra of the ethereal forms.

Oxidative Titrations.—Titrations of the model monomers and the three oligomeric hydroquinones were carried out under conditions which have been described,[1] in 1 and 90% acetic acid. Ceric ammonium nitrate, $Ce(NH_4)_2(NO_3)_6$, was used as the oxidizing agent and was dissolved in the same solvent as was the hydroquinone being titrated. The titration results, *calculated* to the hydrogen electrode scale and *calculated* to pH 0.0 (using the glass electrode to determine the pH of the titrating medium), are shown for 1% acetic acid in Figure 1. The major portions of the curves for 90% acetic acid are almost exactly superimposable on these, except for a displacement of about 20 mv. in a negative direction, and are not shown. The midpoint potentials (E_0) are gathered in Table II. E_0 of unsubstituted hydroquinone was found to be some 60 mv. higher than that of the monosubstituted com-

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(9) A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.*, **23**, 1480 (1955).

(10) L. E. Orgel, *Trans. Faraday Soc.*, **52**, 1172 (1956).

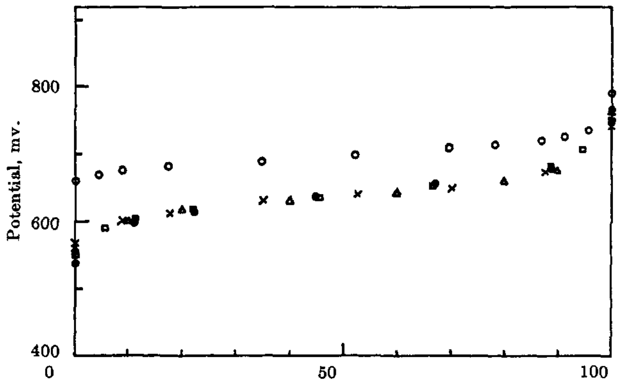

Figure 1.—Titration of hydroquinonyl compounds in 1% acetic acid: ○, hydroquinone; ×, ethylhydroquinone; □, 1,3-bis(2,5-dihydroxyphenyl)propane; △, 1,5-bis(2,5-dihydroxyphenyl)pentane; ●, 1, 3,5-tris(2,5-dihydroxyphenyl)pentane. All points are calculated to the hydrogen scale and pH 0.0.

pound (Table II). This is in accord with the known effect of electron-donating aliphatic substituents.[11] The midpoint potentials of all the monosubstituted hydroquinones in Table II fall within a range of 3 mv. in 1% acetic acid and 7 mv. in 90% acetic acid, and the curves all show the same shape as that of hydroquinone, and all show the index potentials of two-electron curves. Evidently, neither dimerization nor semiquinone formation occurs in significant amounts. The hydroquinonyl functional groups appear to be oxidized independently (within the accuracy of the measurements) and equilibrium was reached rapidly. Thus the *oxidation–reduction behavior* (curve shape, speed of equilibration, and midpoint potential) *of these oligomers is not like that of polyvinylhydroquinone.*

TABLE II

SUMMARY OF MIDPOINT POTENTIALS

Compd.	E_0 in 1% acetic acid, v.	E_0 in 90% acetic acid, v.
Hydroquinone	0.697	0.683
Ethylhydroquinone	0.638	0.618
I	0.640	0.625
II	0.637	0.618
III	0.640	0.621

As was recalled in the first paragraph of this paper, when the polymer is oxidized there is a characteristic change in color from colorless to pink to red to yellow as the oxidation proceeds from 0 to 100%. In all the titrations of oligomers in 90% aqueous acetic acid, the colors of the solutions passed gradually from colorless (hydroquinonyl form) to brilliant yellow (quinonyl form) with degree of oxidation. Excess oxidant increases the intensity of the yellow color, but this becomes important only after the end point has been passed. In 1% aqueous acetic acid, hydroquinone, ethylhydroquinone, and 1,5-bis(2,5-dihydroxyphenyl)-pentane also behaved in this way. However, when 1,3-bis(2,5-dihydroxyphenyl)propane and 1,3,5-tris-(2,5-dihydroxyphenyl)pentane were titrated in the more aqueous solvent, the first addition of oxidizing agent caused the immediate development of a deep red color. The intensity of this color increased to a maximum near the midpoint and then changed gradually to brilliant yellow at 100% oxidation. *Thus, propylene-linked oligomers in highly aqueous solvent seem to have spectral properties in common with vinylhydroquinone homopolymers.* An investigation of this behavior will be reported in a future paper.

Experimental

Elementary microanalyses were carried out by Schwarzkopf and Galbraith Analytical Laboratories. Infrared data were obtained on a Perkin-Elmer Model 421 spectrometer. Infrared samples, as noted in individual cases, were dissolved in analytical grade carbon tetrachloride or suspended in a potassium bromide matrix.

Spectra.—Ultraviolet and visible spectra were measured on a Bausch and Lomb Spectronic 505 spectrometer. Tetrahydrofuran for spectroscopic use was purified by distillation from lithium aluminum hydride[12] under an argon atmosphere and mixed with 5% of its volume of deaerated water. When kept in the dark and under an inert atmosphere of nitrogen or argon, all spectral solutions remained unchanged for at least 24 hr. Exposure of the substituted hydroquinone solutions to air for several minutes caused the appearance of quinonyl absorption at 249 mμ. All of the substituted *p*-benzoquinone solutions were shielded from exposure to strong light, except for the short time during which the spectra were being recorded. When solutions of the monosubstituted quinones were allowed to stand in direct light, their color darkened over a period of several hours as the 249-mμ band became very broad, extending strongly into the visible.

Titrations.—The apparatus used was that described elsewhere.[1,4] Potentials were determined by means of a Leeds and Northrup Speedomax recording potentiometer. Constant temperatures were maintained in thermostatically controlled water baths which were heated or cooled with standard equipment. All solvents were transferred and titrations were carried out under a purified nitrogen or argon atmosphere. Potentials were measured against a saturated calomel electrode which had been calibrated on the hydrogen scale at the constant temperature of the electrode, 29.7 ± 0.02°. Thus, all potentials are reported on the hydrogen scale and have been calculated to pH 0.0. In all titrations, three shiny platinum electrodes were used and a precision range of not exceeding 0.003 v. was required of all data. The calculations neglect effects of ionization and salt errors.[13]

Materials.—All reaction solvents were of reagent grade and, except where indicated, were used without further purification. Hydroquinone was recrystallized several times from benzene–methanol and dried under vacuum (m.p. 172–173°). *p*-Benzoquinone was purified by repeated sublimation (m.p. 115–116°) and stored in an acid-rinsed amber bottle. Ethylhydroquinone and the corresponding quinone were prepared by a previously described method.[14] All other reagents were commercial materials unless noted, freshly distilled or recrystallized before use.

2,2′,5,5′-Tetramethoxychalcone.—Sodium (4 g.) reacted in 100 ml. of dry methanol was added to a hot solution of 21.6 g. (0.12 mole) of 2,5-dimethoxyacetophenone and 20.0 g. (0.12 mole) of 2,5-dimethoxybenzaldehyde in 160 ml. of absolute ethanol.[15] The resulting deep red solution was allowed to stand for 2 hr. while cooling to room temperature and was then poured into 1 l. of cold water. An orange oil separated and was extracted with several portions of ether. The combined extracts were washed thoroughly with water and dried over anhydrous magnesium sulfate, and the solvent was removed *in vacuo*. The residue, 37.8 g. of viscous orange oil, could not be purified by distillation nor induced to crystallize by a variety of techniques at temperatures as low as −20°. Consequently, the product was used in its crude form in the following step. (The crude tetramethoxychalcone yielded a red, crystalline 2,4-dinitrophenyl hydrazone[9] of melting point 233–235° from ethanol–ethyl acetate.)

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[11] L. F. Fieser and M. Fieser, "Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1956, p. 712.

[12] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, p. 292.

[13] F. Hovorka and W. Dearing, *J. Am. Chem. Soc.*, **57**, 446 (1935).

[14] E. Clemmensen, *Ber.*, **47**, 51 (1914).

[15] K. W. Bentley and J. Dominguez, *J. Org. Chem.*, **21**, 1348 (1956).

Anal. Calcd. for $C_{25}H_{24}N_4O_8$: C, 59.05; H, 4.76. Found: C, 59.17; H, 5.03.

2,2',5,5'-Tetramethoxydihydrochalcone.—To a solution of 26.5 g. of crude 2,2',5,5'-tetramethoxychalcone in 220 ml. of absolute ethanol in a Parr shaker bomb was added 1.0 g. of 5% palladized charcoal, using normal precautions. Hydrogen was admitted to a pressure of 60 p.s.i.g. Uptake of 1 equiv. of hydrogen was rapid at 27°, being completed after 2 hr. The catalyst was filtered out and the filtrate was concentrated *in vacuo* at 40–50°. Upon cooling to room temperature, 17.8 g. of nearly white crystals formed. An additional 2.5 g. of product was obtained upon further concentration. Recrystallization from methanol gave 19.5 g. (0.059 mole) of white platelets melting at 79–80°.

Anal. Calcd. for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 69.08; H, 6.75.

An infrared spectrum (CCl_4) showed the characteristic aliphatic carbon–hydrogen peaks at 2950 and 2840 cm.$^{-1}$, carbonyl absorption at 1679 cm.$^{-1}$, and ethereal carbon–oxygen bands at 1228 and 1055 cm.$^{-1}$.

1,3-Bis(2,5-dimethoxyphenyl)propane. A.—Ten grams of amalgamated zinc was prepared[16] and placed in a refluxing solution of 10 ml. of 95% ethanol, 5 ml. of water, and 15 ml. of concentrated hydrochloric acid. Refluxing with vigorous stirring was maintained as 2.5 g. (7.6 mmoles) of 2,2,',5,5'-tetramethoxydihydrochalcone was added and thereafter for an additional 5 hr. The reaction mixture was cooled and the liquid was decanted into an equal volume of water. The product was extracted with ether and washed successively with water, 1 *N* aqueous sodium bicarbonate, and water. Drying over anhydrous magnesium sulfate and removal of solvent left 2.1 g. of a multicomponent red oil. Column chromatography on neutral alumina, with benzene as the mobile phase, satisfactorily isolated the desired product. Zone migrations were conveniently followed by their fluorescence under ultraviolet light. The first fraction eluted, after evaporation of solvent, yielded a colorless oil which solidified upon standing. Recrystallization from methanol gave 0.9 g. (2.8 mmoles) of product, m.p. 61–62° (37% of theory).

Anal. Calcd. for $C_{19}H_{24}O_4$: C, 72.13; H. 7.65. Found: C, 72.05; H, 7.53.

The infrared spectrum (CCl_4) showed aliphatic carbon–hydrogen bands at 2998, 2940, and 2832 cm.$^{-1}$, aromatic in-plane vibrations at 1609 and 1590 cm.$^{-1}$, and ethereal carbon–oxygen at 1220 and 1050 cm.$^{-1}$. (Red intractable oils subsequently eluted from the column were not characterized.)

B.—A solution of 20.0 g. (0.06 mole) of 2,2',5,5'-tetramethoxydihydrochalcone and 0.2 g. of *p*-toluenesulfonic acid monohydrate in 200 ml. of methanol was mixed with 2.0 g. of 5% palladized charcoal in a Parr bomb. With continued shaking, 2 equiv. of hydrogen was consumed within 8 hr. at 30°. The filtered solution was concentrated *in vacuo* to a viscous yellow oil which was taken up in ether, washed with 1 *N* aqueous sodium bicarbonate and then water, and dried over anhydrous magnesium sulfate. Removal of solvent left a solid residue which, recrystallized from a methanol–ether mixture, yielded 12.0 g. (0.038 mole) of product (63% of theory). Comparative infrared spectra, melting points, and mixture melting point showed that the products obtained by methods A and B were identical.

1,3-Bis(2,5-dihydroxyphenyl)propane. A.—A solution of 2.52 g. (8.0 mmoles) of 1,3-bis(2,5-dimethoxyphenyl)propane in 150 ml. of dry, thiophene-free benzene was treated with 25 g. of anhydrous aluminum bromide and stirred under reflux for 8 hr. in a dry atmosphere. Excess aluminum bromide was hydrolyzed with water and the product was extracted with tetrahydrofuran. Slightly pink hygroscopic needles (1.60 g., 6.2 mmoles) were obtained upon recrystallization of the crude product from a methanol–benzene mixture (77% of theory). Further purification by sublimation (0.001 mm. and 180–190°) gave an analytically pure, white sample of m.p. 211° dec.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 68.92; H, 6.36.

The infrared spectrum (KBr) showed a strongly associated hydroxyl hydrogen–oxygen stretching at 3350 cm.$^{-1}$ (broad), aromatic carbon–hydrogen stretching at 2938 and 2862 cm.$^{-1}$, aromatic in-plane vibration at 1500 cm.$^{-1}$, and carbon–oxygen stretching at 1362 and 1334 cm.$^{-1}$.

B.—One gram (3.2 mmoles) of 1,3-bis(2,5-dimethoxyphenyl)propane and 12.0 g. of dry pyridine hydrochloride were heated to 180–200° for 3 hr. under a dry nitrogen atmosphere with continuous stirring. After cooling, the solid reaction mixture was dissolved in 20 ml. of deaerated water and the product was extracted with tetrahydrofuran. The combined extracts were washed successively with five portions of sodium chloride saturated 2 *N* hydrochloric acid, two portions of saturated aqueous sodium chloride, a solution of sodium hydrosulfite in dilute aqueous sodium bicarbonate, and once more with saturated aqueous sodium chloride. The extract was dried over anhydrous magnesium sulate and the solvent was removed. The solid residue, upon recrystallization from methanol–benzene, gave 0.64 g. (2.5 mmoles) of pink needles (78% of theory). After sublimation, the product was shown by comparative spectra, melting points, and mixture melting point to be identical with that obtained by the alternate procedure.

1,3-Bis(*p*-benzoquinonyl)propane.—One gram of anhydrous sodium sulfate and 1.16 g. of freshly prepared silver oxide were stirred for 30 min. with 0.50 (1.9 mmoles) of 1,3-bis(2,5-dihydroxyphenyl)propane in 10 ml. of dry, freshly purified tetrahydrofuran.[12] After filtration and removal of solvent, the residue was sublimed (0.2 mm. and 120°) and gave 0.25 g. (1.0 mmole) of a yellow powder which melted at 149–150° (53% of theory).

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.13; H, 4.96.

The infrared spectrum (KBr) showed vinylic and aliphatic carbon–hydrogen peaks at 3056 and 2955 cm.$^{-1}$ and olefinic carbon–carbon stretching at 1595 and 960 cm.$^{-1}$, all characteristic of the desired product.

Catalytic hydrogenation of the product at 15 p.s.i.g. with 5% palladized charcoal in ethyl acetate regenerated the corresponding bis(hydroquinone) in quantitative yield. A refluxing methanolic solution of 0.2 g. of the hydrogenation product and 1.0 g. of freshly distilled dimethyl sulfate was treated with a slight excess of saturated methanolic potassium hydroxide. The reaction mixture was diluted with water and the product was extracted with ether. Drying over potassium hydroxide pellets and removal of solvent left a yellow oil which crystallized upon standing. Recrystallization from methanol gave a material melting at 61–62°. A mixture melting point with 1,3-bis(2,5-dimethoxyphenyl) propane showed no depression. Infrared spectra (CCl_4) of both samples were identical.

1,3-Bis(2,5-dimethoxybenzoyl)propane.—A mixture of 55.0 g. (0.42 mole) of anhydrous aluminum chloride in 200 ml. of dry, freshly distilled carbon disulfide was cooled to 0° under the usual Friedel–Crafts conditions. After 55.0 g. (0.40 mole) of dry *p*-dimethoxybenzene was dissolved in the chilled mixture, a solution of 25.0 g. (0.15 mole) of glutaryl chloride in 100 ml. of dry carbon disulfide was added, with efficient stirring, over a period of 2 hr. The resulting black, tarry mixture was stirred for an additional 3 hr. at 0° and allowed to warm and to stand at room temperature for 13 hr. Crushed ice (500 ml.) and 40 ml. of concentrated hydrochloric acid were added to hydrolyze the aluminum complex. The layers were separated and the aqueous fraction was extracted with ether. After combining and washing the extracts successively with water, 10% aqueous potassium carbonate, and saturated sodium chloride, the solvent was removed *in vacuo*. Unreacted *p*-dimethoxybenzene was removed by steam distillation. Upon standing, the yellow, oily residue solidified. Recrystallization from methanol gave 38.0 g. (0.10 mole) of white product melting at 64–65° (67% of theory).

Anal. Calcd. for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50. Found: C, 67.66; H, 6.50.

The infrared spectrum (CCl_4) showed characteristic carbon–hydrogen stretching bands, aromatic at 3006 and aliphatic at 2950, 2912, and 2840 cm.$^{-1}$, carbonyl absorption at 1675 cm.$^{-1}$, and ethereal carbon–oxygen peaks at 1222 and 1046 cm.$^{-1}$.

1,5-Bis(2,5-dimethoxyphenyl)pentane.—Ten grams (0.027 mole) of 1,3-bis(2,5-dimethoxybenzoyl)propane and 1.0 g. of 10% palladized charcoal were taken up in 50 ml. of glacial acetic acid. The mixture was heated to 80° in a Parr shaker bomb which was equipped with an external heating coil and thermocouple and hydrogen was admitted to a pressure of 60 p.s.i.g. Four equivalents of hydrogen was taken up within 6 hr. at 80°. The cooled mixture was filtered and the filtrate was poured into 300 ml. of water containing an excess of sodium carbonate. The product was extracted with ether, washed with dilute aqueous sodium bicarbonate and then with saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, and evaporated to dryness. Recrystallization of the solid residue from

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(16) E. L. Martin, *Org. Reactions*, **1**, 163 (1942).

methanol yielded 5.30 g. (0.015 mole) of pure white product of melting point 47–48° (57% of theory).

Anal. Calcd. for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19. Found: C, 72.79; H, 8.30.

An infrared spectrum (CCl_4) showed aromatic and aliphatic carbon–hydrogen stretching absorptions at 3003 and 2940, 2915, 2865, and 2840 cm.$^{-1}$ respectively, aromatic in-plane vibrations at 1605, 1590, and 1500 cm.$^{-1}$, and ethereal carbon–oxygen bands at 1222 and 1050 cm.$^{-1}$.

1,5-Bis(2,5-dihydroxyphenyl)pentane.—Five grams (0.015 mole) of 1,5-bis(2,5-dimethoxyphenyl)pentane and 35.0 g. of dry pyridine hydrochloride were heated to 180–200° under a dry nitrogen atmosphere for 3 hr. with continuous stirring. Work-up was as described above for 1,3-bis(2,5-dihydroxyphenyl)propane. Evaporation of the dried tetrahydrofuran solution left a dark viscous oil which solidified upon warming with benzene containing a trace of methanol. Pearly white platelets (3.78 g., 0.013 mole), m.p. 165–166°, were obtained upon recrystallization from benzene containing a trace of methanol (88% of theory). Recrystallization from this mixture was best effected by taking the solid up in as little methanol as possible and filtering the resulting solution into a large volume of boiling benzene.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.61; H, 6.78.

The infrared spectrum (KBr) showed strongly associated hydroxyl oxygen–hydrogen stretching at 3200 cm.$^{-1}$ (broad), aliphatic carbon–hydrogen stretching at 2945, 2930, and 2855 cm.$^{-1}$, aromatic in-plane vibration at 1616 and 1510 cm.$^{-1}$, and carbon–oxygen stretching at 1190 cm.$^{-1}$.

1,5-Bis(*p*-benzoquinonyl)pentane.—A solution of 5.0 g. (0.018 mole) of 1,5-bis(2,5-dihydroxyphenyl)pentane in 100 ml. of freshly purified tetrahydrofuran was stirred for 30 min. with 5.0 g. of anhydrous sodium sulfate and 12.0 g. of silver oxide. After filtration and removal of solvent, 4.60 g. of crude yellow solid remained. Upon recrystallization from absolute ethanol, 3.98 g. (0.014 mole) of brilliant yellow needles, m.p. 84.5–85.5°, was obtained (80% theory).

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.76; H, 5.67.

An infrared spectrum (KBr) showed vinylic and aliphatic carbon–hydrogen stretching peaks at 3055 and at 2930 and 2860 cm.$^{-1}$, respectively, carbonyl absorption at 1650 cm.$^{-1}$, and olefinic carbon–carbon stretching at 918 cm.$^{-1}$.

Hydrogenation of the product and remethylation in the manner described above gave 1,5-bis(2,5-dimethoxyphenyl)pentane, as further proof of structure.

1,3,5-Tris(2,5-dimethoxyphenyl)-3-pentanol.—Using the normal precautions, 10.0 g. (0.041 mole) of β-bromoethyl-2,5-dimethoxybenzene[17] in 60 ml. of anhydrous ether was added slowly to 0.96 g. (0.041 g.-atom) of iodine-activated magnesium metal. External warming was required to initiate and maintain the reaction. When nearly all of the metal was consumed, the reaction vessel was equipped with a modified Soxhlet extractor containing 11.5 g. (0.035 mole) of 2,2′,5,5′-tetramethoxydihydrochalcone (which is relatively insoluble in cold ether). Refluxing with vigorous stirring was maintained as the ketone was washed into the Grignard solution. After refluxing for an additional hour and then cooling, the product complex was hydrolyzed by the slow addition of 100 ml. of cold, saturated aqueous ammonium chloride. Separation of the layers, extraction of the aqueous layer with ether, drying of the combined extracts over anhydrous magnesium sulfate, and removal of solvent left a viscous yellow oil which crystallized from absolute ethanol. Recrystallization gave 12.58 g. (0.025 mole) of white platelets, m.p. 82–83° (73% of theory).

Anal. Calcd. for $C_{29}H_{36}O_7$: C, 70.14; H, 7.31; mol. wt., 496.6. Found: C, 69.91; H, 7.17; mol. wt., 486 (Rast).

An infrared spectrum (CCl_4) showed the characteristic hydroxyl absorptions at 3625 (unbonded) and 3550 cm.$^{-1}$ (bonded), aromatic carbon–hydrogen stretching at 3005 cm.$^{-1}$, and aliphatic carbon–hydrogen at 2950, 2915, and 2840 cm.$^{-1}$. Aromatic in-plane vibrations appeared at 1605, 1544, and 1499 cm.$^{-1}$, and ethereal carbon–oxygen bond stretching at 1220 and 1046 cm.$^{-1}$.

1,3,5-Tris(2,5-dimethoxyphenyl)-2-pentene.—A small crystal of iodine was dissolved in 50 ml. of *m*-xylene in a flask equipped for distillation. 1,3,5-Tris(2,5-dimethoxyphenyl)-3-pentanol (3.0 g., 6.05 mmoles) was added and the mixture was heated to reflux under a nitrogen atmosphere. As the boiling point of the solvent was approached, a vigorous reaction took place and water was rapidly azeotroped out. Distillation was continued until the distillate became clear. The yellow residue was cooled, washed with dilute aqueous sodium carbonate, 5% aqueous sodium thiosulfate, and saturated aqueous sodium chloride successively, dried over anhydrous magnesium sulfate, and evaporated to dryness *in vacuo.* The solid residue, which was recrystallized from methanol, consisted of 2.16 g. (4.52 mmoles) of white solid melting at 98–99° (75% of theory).

Anal. Calcd. for $C_{29}H_{34}O_6$: C, 72.78; H, 7.16. Found: C, 72.73; H, 7.12.

An infrared spectrum showed carbon–hydrogen stretchings at 3075, 3036, 3005, 2955, 2915, and 2840 cm.$^{-1}$, aromatic in-plane vibrations at 1606, 1590, and 1499 cm.$^{-1}$, and ethereal carbon–oxygen bonds at 1228 and 1050 cm.$^{-1}$.

1,3,5-Tris(2,5-dimethoxyphenyl)pentane.—Hydrogenation of 6.2 g. (0.013 mole) of the tris-substituted pentene with 1.0 g. of 5% palladized charcoal in 70 ml. of ethyl acetate at 60 p.s.i.g. and 25° for 10 hr. gave a colorless oil on work-up. Taken up in a methanol–ether mixture, the oil crystallized at 0° to give a nearly quantitative yield of 6.04 g. of white product of m.p. 56–57°.

Anal. Calcd. for $C_{29}H_{36}O_6$: C, 72.47; H, 7.55. Found: C, 72.50; H, 7.75.

The infrared spectrum (CCl_4) showed aromatic carbon–hydrogen stretching at 3040 and 3002 cm.$^{-1}$, aliphatic carbon–hydrogen at 2948, 2912, and 2838 cm.$^{-1}$, aromatic in-plane vibrations at 1605, 1538, and 1499 cm.$^{-1}$, and ethereal carbon–oxygen at 1220 and 1050 cm.$^{-1}$.

1,3,5-Tris(2,5-dihydroxyphenyl)pentane.—Four grams (8.4 mmoles) of the tris(hydroquinone dimethyl ether) was heated with 50 g. of pyridine hydrochloride in the previously described manner. Evaporation of the purified tetrahydrofuran extract solution left an extremely viscous glass which, under vacuum, expanded to a spongy, hygroscopic amorphous solid. Crude product (2.85 g.) was obtained but could not be induced either to crystallize or sublime. A satisfactory elementary analysis could not be obtained on this material. The product was purified by an indirect route involving oxidation to the easily purified tris-(*p*-benzoquinone) and hydrogenation.

1,3,5-Tris(*p*-benzoquinonyl)pentane.—Two grams (5.1 mmoles) of crude 1,3,5-tris(2,5-dihydroxyphenyl)pentane in 30 ml. of tetrahydrofuran was oxidized with silver oxide and worked up as previously described. Product (1.42 g., (3.6 mmoles) of melting point 122–123° was obtained upon recrystallization of the crude residue from absolute ethanol (71% of theory).

Anal. Calcd. for $C_{23}H_{18}O_6$: C, 70.76; H, 4.65. Found: C, 70.89; H, 4.86.

In the infrared spectrum (KBr) there appeared carbon–hydrogen stretching absorptions at 3058 and 2980 cm.$^{-1}$, a carbonyl band at 1650 cm.$^{-1}$, and other intense bands at 1291, 1078, and 910 cm.$^{-1}$.

Regeneration of 1,3,5-Tris(2,5-dihydroxyphenyl)pentane.—A solution of 0.39 g. (1.0 mmole) of 1,3,5-tris(*p*-benzoquinonyl)-pentane in 25 ml. of glacial acetic acid containing 0.1 g. of 10% palladized charcoal was hydrogenated at 1 atm. and 25°. The calculated volume of hydrogen was consumed within 30 min. The catalyst was carefully filtered out on a layer of infusorial earth in a nitrogen atmosphere and the colorless filtrate was immediately freeze dried. The white powdery residue was separated from the last traces of solvent and water in a vacuum desiccator over potassium hydroxide pellets and phosphorus pentoxide. The product did not have a sharp melting point, but appeared to soften at 70–80°.

Anal. Calcd. for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 69.27; H, 6.39.

The infrared absorption spectrum (KBr) showed a broad hydroxyl absorption centered at 3350 cm.$^{-1}$, aromatic carbon–hydrogen stretching at 3060 and 3030 cm.$^{-1}$, aliphatic carbon–hydrogen stretching at 2935 and 2860 cm.$^{-1}$, aromatic in-plane vibrations at 1600 and 1496 cm.$^{-1}$, and phenolic carbon–oxygen at 1185 cm.$^{-1}$.

Treatment of the product which had been purified in this manner with an alkaline alcoholic solution of dimethyl sulfate, as

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[17] J. Green, D. McHale, S. Marcinkiewicz, and P. R. Watt, *J. Chem. Soc.*, 3362 (1959).

[18] J. M. Church, F. C. Whitmore, and R. V. McGrew, *J. Am. Chem. Soc.*, **56**, 176 (1934).

described above, regenerated the corresponding tris(hydroquinone dimethyl ether) in good yield.

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Condensation of Aromatic Nitro Compounds with Arylacetonitriles. VII. Some Studies Concerning the Reduction of Phenylcyanomethylenequinone Oximes[1,2]

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Raney nickel catalyzed reduction of phenylcyanomethylenequinone oxime at room temperature in the presence of ammonia or aliphatic amines produces *p*-aminobenzophenone as the major product. Similar reductions in the presence of other nucleophilic reagents produce *p*-aminophenylphenylacetonitrile. A mechanism for the formation of *p*-aminobenzophenone is offered. The catalytic and chemical reductions of six arylcyanomethylenequinone oximes in the presence of diethylamine are described and compared.

It was previously reported[3] that the catalytic reduction of phenylcyanomethylenequinone oxime, or more properly 4-oxo-α-phenyl-2,5-cyclohexadien-$\Delta^{1,\alpha}$-acetonitrile oxime, using hydrogen and Raney nickel in methanol at room temperature yielded *p*-aminophenylphenylacetonitrile. We have now found that similar reductions of the same compound in the presence of ammonia or aliphatic amines followed by treatment with water produce *p*-aminobenzophenone as the major product. Reactions in like manner in the presence of aniline, pyridine, potassium hydroxide, and other nucleophilic reagents yielded *p*-aminophenylphenylacetonitrile. It should be noted that one reduction conducted in the presence of both potassium hydroxide and diethylamine gave 2,3-bis(4′-aminophenyl)-2,3-diphenylsuccinonitrile. The results of these experiments are summarized in Table I.

It is interesting to speculate concerning the mechanism whereby *p*-aminobenzophenone is produced. Certainly the formation of this product is dependent upon the presence of an amino function of sufficient basicity such as is provided by ammonia and aliphatic amines. Basicity alone is not the determining factor, since the use of potassium hydroxide fails to produce *p*-aminobenzophenone. The relative basicity of the amino function, however, is a determining factor, since the use of aniline and pyridine likewise fails to produce the ketone in a detectable amount.

A reduction step apparently takes place prior to an attack by water or other nucleophile. We propose a reduction as the first step in the mechanism because we have found that phenylcyanomethylenequinone oxime (**1**) fails to react with ammonia alone, with ammonia in methanol, with diethylamine alone, with diethylamine in methanol, and with diethylamine in methanol in the presence of Raney nickel, followed by treatment with water. We further propose that phenylcyanomethylenequinone oxime (**1**) is first reduced to phenylcyanomethylenequinonimine (**2**), or more accurately 4-imino-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile.

Table I

Catalytic Reductions of Phenylcyanomethylenequinone Oxime Using Raney Nickel, Hydrogen, and Methanol in the Presence of Nucleophilic Reagents at Room Temperature

Nucleophilic reagent	Major product
Ammonia	4-Aminobenzophenone
n-Butylamine	4-Aminobenzophenone
n-Butylamine[a]	4-Aminobenzophenone
Diethylamine	4-Aminobenzophenone
Piperidine	4-Aminobenzophenone
Triethylamine	4-Aminobenzophenone
Aniline	4-Aminophenylphenylacetonitrile
Pyridine	4-Aminophenylphenylacetonitrile
Potassium hydroxide	4-Aminophenylphenylacetonitrile
Potassium phenolate	4-Aminophenylphenylacetonitrile
Potassium acetate	4-Aminophenylphenylacetonitrile
Potassium iodide	4-Aminophenylphenylacetonitrile
Potassum hydroxide and diethylamine	2,3-Bis-(4′-aminophenyl)-2,3-diphenylsuccinonitrile
Potassium hydroxide and pyridine	4-Aminophenylphenylacetonitrile
Potassium acetate and diethylamine	4-Aminobenzophenone

[a] No methanol was used in this reduction.

It seems that the second step in the mechanism is an attack by water or other nucleophile on the intermediate imine **2**, followed by the elimination of hydrogen cyanide. Eventually there must be an attack by water. However, since the reduction mixtures contain trace amounts of water at most, it is not illogical to postulate an intermediate attack by the amine compound or by methanol, with subsequent displacement by water. The over-all result may be pictured as an amino-catalyzed attack by water, followed by elimination of hydrogen cyanide.

Finally, the amino compound plays an essential role in the production of *p*-aminobenzophenone (**4**) over and above its role as catalyst in the attack by water; otherwise the reactions in the presence of other bases such as potassium hydroxide, potassium phenolate, or potassium acetate should have produced the

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(1) Previous paper: *J. Chem. Eng. Data*, **8**, 580 (1963).

(2) This research was supported in part by National Science Foundation Grant G19165.

(3) R. B. Davis and J. D. Benigni, *J. Chem. Eng. Data*, **8**, 578 (1963).