Wolff–Kischner Reduction of Acetoxydione XIIa.—The acetoxydione XIIa obtained by Jones oxidation[5] of 0.100 g of thurberogenin monoacetate (Xa) was subjected to modified Wolff–Kischner reduction[12a] as described in the preceding experiment. The reaction product, after work-up, was chromatographed on basic alumina (activity I). A fraction containing a major, more mobile and a small, minor, less mobile compound (tlc, 4:1 benzene–methanol) was obtained from the 3:2 ether–chloroform eluates. Preparative tlc (4:1 benzene–methanol) on this fraction furnished the major component as a pale yellow oil, 0.069 g, which crystallized on trituration with methanol. The product, although homogeneous by tlc, melted over a wide range, which behavior was not significantly altered by recrystallization. After three recrystallizations from methanol, it had mp 106–137°. The infrared spectrum (KBr pellet) of this material, however, was superimposable on that of authentic 3-deoxybetulin (XVI), and its mass spectrum (m/e 426) was identical in every detail with that of authentic XVI. The 3-deoxybetulin obtained from XIIa is apparently a mixture of C-19 epimers.

ORD Spectral Data Pertaining to the Stereochemistry at C-19. A. Methyl-3-acetoxy-30-nor-20-ketobetulinate (XVII).—The preparation of this compound has been described previously.[7] It exhibited the following ORD spectrum (c 0.087, dioxane): $[\Phi]_{305}$ +1368 (peak), $[\Phi]_{260}$ −1938° (trough).

B. Thurberogenintriol Triacetate 30-Nor 20-Ketone (XX).—This compound was prepared by a method similar to that described[7] for the preparation of XVII. It exhibited the following ORD spectrum (c 0.033, dioxane): $[\Phi]_{589}$ 0°, $[\Phi]_{305}$ +1848° (peak), $[\Phi]_{257}$ −2184° (trough).

C. Methyl 20-Keto-19-methoxy-30-norbetulinate (XXIIa).—The preparation of this compound (the "E-homo" derivative) has been described previously.[6] It exhibited the following ORD spectrum (c 0.045, dioxane): $[\Phi]_{589}$ 0°, $[\Phi]_{306}$ +1601° (peak), $[\Phi]_{255}$ −3937° (trough).

Attempted Double-Bond Isomerization of Hydroxydione XII.—A sample (ca. 20 mg) of XII was heated at reflux in a solution of 1.50 g of sodium methoxide in 20 ml of methanol. Aliquots for ultraviolet examination were withdrawn periodically during a 24-hr period, but the generation of any significant chromophore in the 240 mμ region was not observed. The major component of the reaction mixture after 24 hr was indicated to be unchanged starting material by tlc (4:1 benzene–methanol) examination.

Registry No.—III, 13950-48-6; IV, 13950-49-7; V, 13950-50-0; X, 13950-51-1; Xa, 13950-52-2; XII, 13952-73-3; XIIa, 13952-74-4; XIVa, 4356-31-4; XV, 13952-75-5; XVI, 13952-76-6; XX, 13952-77-7.

Electron-Transfer Polymers. XXXI. Preparation of Difunctional Benzoquinones and Related Derivatives and Polymers

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Received May 11, 1967

Synthesis of three 1,4-benzoquinonediols and their derivatives is described. It is shown that these diols form redox polymers through polycondensation reactions in which the quinone group need not be protected. As examples, syntheses of two polyesters and a polyurethane are described. A redox polyester could also be prepared from hydroquinonediacetic acid and 1,4-butanediol. Model compounds for these polyesters show that the ester bond is quite stable under suitable oxidative conditions.

The redox system hyrdoquinone–quinone is completely reversible. When one attempts to install this system in a polymeric structure, and then to describe its reactions, one is faced with certain problems.

(1) One or two functional groups must be introduced into the hydroquinone molecule to make it reactive in a polymerization reaction. This reaction must be such that it takes place at the functional group only and does not involve the hydroquinone or quinone functions in a side reaction. For example, vinylhydroquinone cannot be successfully polymerized[1] because the free hydroquinone group is a strong inhibitor for radical and ionic polymerizations. This difficulty is overcome either by protecting both phenolic hydroxyls with acetyl, benzoyl, ethoxy ethyl, or ether groups,[1] or to some extent by protecting *one* of the hydroxyls with an ether group.[2] The protected monomers can then yield high molecular weight polymers.

(2) The redox units in the resulting polymer are now protected, but the protecting groups must be removed without cross-linking the polymer and without damaging the very reactive redox groups. Depending on the nature of the protecting group it is more or less possible to prepare polymeric redox systems in this way.[1] However, it would be a major improvement to find polymerization reactions that avoid the problem of the protecting groups. (3) The redox properties of the polymers differ in some respects from those of hydroquinone.[3] This behavior, explainable as a kind of neighboring group effect in which internal electron transfer occurs between redox groups under the drive of internal quinhydrone formation[4] complicates the interpretation of the behavior of the polymers as electron exchangers and redox catalysts.

These considerations led us away from polyaddition toward polycondensation reactions. It is known that high molecular weight polymers can be obtained by treating diacyl chlorides with diols at very low temperatures in the presence of a suitable base.[5] The reaction of diols with diisocyanates at low temperature leads to polyurethanes.[6] Both reactions, as well as esterification of diacids with diols, should be suitable for our purposes if applied to quinone derivatives because the quinone group is quite stable under the conditions at which these polymerizations take place. Some redox polymers have been made by polycondensation.[7] We report a systematic study of some quin-

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

[2] N. Nakabayashi, G. Wegner, and H. G. Cassidy, *J. Polymer Sci.* (submitted).

[3] I. D. Robinson, M. Fernandez-Refojo, and H. G. Cassidy, *ibid.*, **39**, 47 (1959).

[4] R. E. Moser and H. G. Cassidy, *J. Org. Chem.* **30**, 3336 (1965); R. E. Moser, Ph. D. Dissertation, Yale University, 1965.

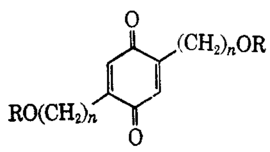
[5] P. W. Morgan and S. Kwolek, *J. Polymer Sci.*, **A2**, 181, 209 (1964); S. Kwolek and P. W. Morgan, *ibid.*, **A2**, 2693.

[6] W. R. Sorenson and F. W. Campbell, "Preparative Methods of Polymer Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

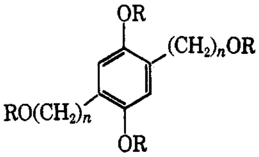
[7] The literature is reviewed in ref 1.

onediols and of their ability to form redox polymers by polycondensation. Our aim here is to be able to control accurately the distance between the redox functional groups in the polymer (in terms of the number of atoms intervening in the polymer chain) and thus to extend the series already begun by Moser and Cassidy.[4,8] This will enable further investigation of the unusual properties of redox polymers referred to above.

To obtain quinonediols with the structure I (R = H), one starts best from the corresponding diacid derivative III (R = C_2H_5) which upon reduction with lithium aluminum hydride yields the hydroquinonediol II (R = H). This is easily oxidized to the quinonediol I (R = H) without attacking the alcohol groups. In this manner 2,5-bis(hydroxymethyl)hydroquinone (IIa) was prepared by reduction of the 2,5-dihydroxyterephthalic ester IIIa[9] in boiling tetrahydrofuran (THF). This hydroquinone, which might also be prepared by condensation of hydroquinone with formaldehyde under carefully controlled conditions,[10] was obtained in 75% yield. Very insoluble in most organic solvents, it was recrystallized from a mixture of dimethylformamide and ether. Heat and light induce rapid decomposition. By reaction with acetyl chloride in pyridine–THF it was converted to IIb. Oxidation of IIa with silver oxide in THF at room temperature gave 2,5-bis(hydroxymethyl)benzoquinone (Ia) in good yield. All quinones of this type are soluble in polar solvents such as THF, DMF, DMSO, pyridine, alcohols, and acetic acid and are poorly soluble in hydrocarbons and ether.



Ia, n = 1; R = H
b, n = 2; R = H
c, n = 3; R = H
d, n = 1; R = $COCH_3$
e, n = 2; R = $COCH_3$
f, n = 3; R = $COCH_3$
g, n = 3; R = $CONHC_6H_5$



IIa, n = 1; R = H
b, n = 1; R = $COCH_3$
c, n = 2; R = H
d, n = 2; R = $COCH_3$
e, n = 3; R = H
f, n = 3; R = $COCH_3$

Attempts to prepare 2,6-bis(hydroxymethyl)-1,4-benzoquinone (IV) by oxidation of 2,6-bis(hydroxymethyl)-4-methoxyphenol (V)[11] were unsuccessful. Instead of the expected quinone IV, 2,6-bis(formyl)-4-methoxyphenol (VI) was isolated. It was identified by its nmr spectrum, melting point, and derivative. This result is especially interesting because alcoholic groups are usually not oxidized under conditions where *p*-alkoxyphenols and hydroquinones are converted to the corresponding quinones. It has been shown, however, that the substitution pattern of various *p*-alkoxyphenols has a marked effect on the structure of the oxidation product.[12] Depending on solvent and oxidizing agent a variety of products can be formed. Pending evidence for the mechanism of this reaction we add it to the pool of as yet unexplained oxidation reactions of *p*-alkoxyphenols.

The hitherto unknown 2,5-bis(2′-hydroxyethyl)hydroquinone (IIc) was prepared similarly to IIa by reduction of the ethyl ester IIIb[13] in good yield. IIc was easily oxidized by stirring its solution with silver oxide and anhydrous magnesium sulfate in THF. The 2,5-bis(2′-hydroxyethyl)-1,4-benzoquinone was obtained in almost quantitative yield. IIc was readily converted by the described procedure to the tetraacetate IId. Attempts to prepare IIc by directly reducing the free acid IIIc[13] failed even on prolonged heating because of the insolubility of the acid in THF. Even the methyl ester IIId is too insoluble to give good results, whereas the reduction of the ethyl ester IIIb proceeds smoothly.

Preparation of the previously unknown 2,5-bis(3′-hydroxypropyl)-1,4-benzoquinone (Ic) proceeded from the known 2,5-bis(chloromethyl)-1,4-dimethoxybenzene[14] (VII) by a standard malonic ester synthesis. The product, VIII, was obtained in 83% yield as a white crystalline compound. On boiling for 9 hr with hydrobromic acid VIII yielded in one step 90% of IIIe, as a brownish material readily crystallizable from hot water or a mixture of THF and *n*-heptane. Conversion of crude IIIe to the ethyl ester IIIf, and reduction as before in a smooth reaction yielded 66% of white crystalline IIe. IIe gave a tetraacetate. Oxidation of IIe as before yielded Ic.

In model reactions the quinonediols Ia, Ib, and Ic readily yielded almost quantitatively the corresponding diacetates when reacted with acetyl chloride in THF in the presence of a small excess of pyridine, thus showing that this reaction may be run without damaging the quinone nucleus. Carrying out the reaction with Ib, using sebacoyl chloride, and terephthaloyl chloride yielded the polymers. The polyester from sebacoyl chloride was a deep yellow, waxy mass, was soluble in many organic solvents, and has a η_{sp}/c value of 9.2 (cm^3/g) in dioxane at 26°. The infrared spectrum showed the expected bands of a polyester at 1729 (C=O stretching), 1172 (C—O stretching), and a quinone at 1654 cm^{-1}.[15] This supports the assignment of structure IX for this polymer. The polyester from terephthaloyl chloride was a yellow powder, very insoluble in most organic solvents and soluble only in hot dimethylformamide and hot dimethyl sulfoxide. This behavior is not unexpected of this type of polyester. The infrared spectrum showed bands expected of a terephthalic ester[15] at 1740 (C=O stretching), 1278 and 1130 (C—O stretching), and at 1655 cm^{-1} (quinone). This supports the structure X for this polymer.

In a model reaction, Ic was treated with phenyl isocyanate in THF with triethylamine as the catalyst. The corresponding bisurethane (Ig) was obtained in good yield, thus establishing the feasibility of the reactions. When Ic was treated under the same conditions with methylenebis(4-phenyl isocyanate), the polyurethan, a yellow solid, was formed in quantita-

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(10) H. von Euler, E. Adler, H. Hasselquist, and M. Lundin, *Arkiv Kemi, Minerol., Geol.*, **18A**, No. 7 (1944); *Chem. Abstr.*, **39**, 3786.7 (1945).

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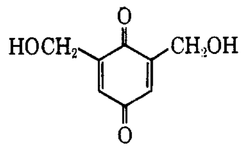
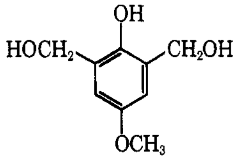
CHART I



IV



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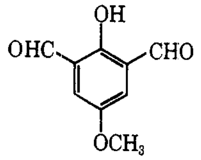

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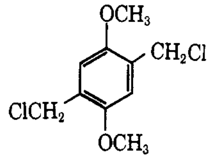

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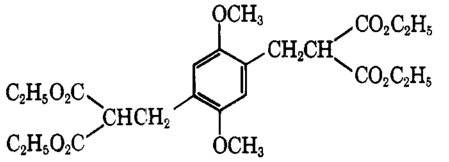

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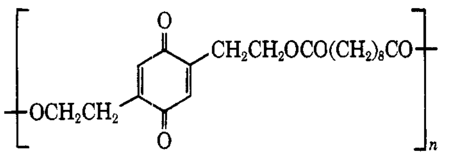

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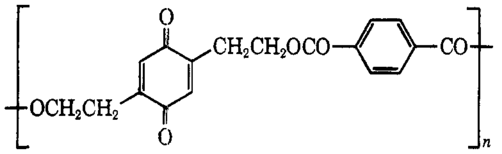
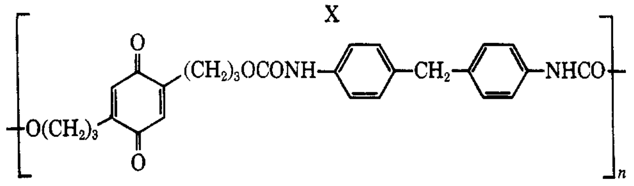


X



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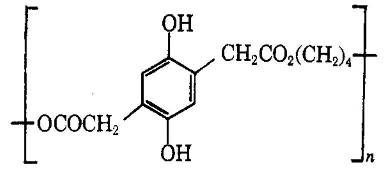
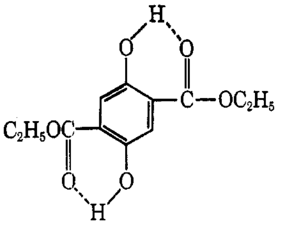


XII

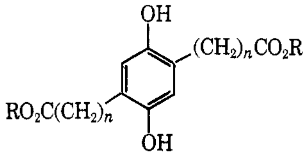


XIV

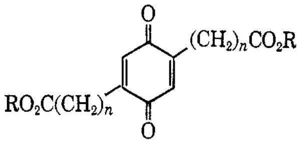
tive yield. Its viscosity in dioxane at 26° was η_{sp}/c = 18.0 (cm^3/g). The infrared spectrum showed bands at 1725 and 1540 (amide-I and amide-II bands[15]) and at 1654 cm^{-1} (quinone). This supports the use of structure XI for this polymer.

As a third polymerization reaction, IIIc was esterified by 1,4-butanediol under acidic conditions. This should yield a linear polymer since the phenolic hydroxyl does not participate in ester formation under acidic conditions. By heating together equimolar amounts of the components in toluene in the presence of p-toluenesulfonic acid and antimonous oxide,[16] distilling off the toluene while it was slowly replaced with xylene, polyester was obtained in about 50% yield (after purification) as a brittle material with a viscosity value of η_{sp}/c = 8.7 (cc/g) in dimethylformamide at 26°. The infrared spectrum showed bands at 1725 and 1190 due to the ester, and a rather broad phenolic hydroxyl band at 3420 cm.$^{-1}$. The data support the assignment of structure XII for this polymer.

The ester function appears to be perfectly stable under controlled reaction conditions. Thus the hydroquinone diesters IIIb, IIId, and IIIf could be oxidized in nearly quantitative yield to the benzoquinone diesters XIIIa, XIIIb, and XIIIc. It was not possible, however, to oxidize 2,5-dihydroxyterephthalic ester (IIIa) by such agents as ferric chloride, silver oxide, hydrogen peroxide, or lead tetraacetate. A variety of solvents were investigated. Either decomposition materials or, more usually, pure starting material was retrieved. It would appear that very strong hydrogen bonding prevents radical abstraction of the phenolic hydrogen. This explanation is supported by the shift to low field observed for the phenolic hydrogen in the nmr. It gives a signal at δ 10.08 (in CDCl$_3$) which implies very strong interaction as shown in structure XIV. A polyester incorporating a structure of this kind is therefore not useful as a redox polymer.



IIIa, $n = 0$; $R = C_2H_5$
b, $n = 1$; $R = C_2H_5$
c, $n = 1$; $R = H$
d, $n = 1$; $R = CH_3$
e, $n = 2$; $R = H$
f, $n = 2$; $R = C_2H_5$



XIIIa, $n = 1$; $R = C_2H_5$
b, $n = 1$; $R = CH_3$
c, $n = 2$; $R = C_2H_5$

Further work is in progress to evaluate the redox and spectral properties of the 31 polymers and model compounds described above.

Structures IV–XII and XIV are shown in Chart I.

Experimental Section[17]

Materials.—All reaction solvents were of reagent grade and, except as indicated, were used without further purification. All other reagents were commercial materials, freshly distilled or recrystallized before use, unless noted.

Methods.—Wherever possible, the general methods are described, with notes of special conditions, followed by the description of the compounds prepared by them. It must be remem-

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[16] H. R. Billica, U. S. Patent 2,647,885 (1953); *Chem. Abstr.*, **47**, 10278*d* (1953).

[17] Elementary microanalyses were carried out by Galbraith Analytical Laboratories. Infrared data were obtained with a Perkin-Elmer Model 421 spectrometer, the sample being dissolved in a potassium bromide matrix; nmr data were obtained with a Varian Associates Model A-60 spectrometer. The chemical shifts are given in δ values, the letters within the brackets having the meaning s, singlet; d, doublet; tr, triplet; qu, quadruplet; and m, multiplet. Analytical grade deuteriochloroform, carbon tetrachloride, pyridine, acetonitrile, or dimethyl sulfoxide were used as solvents. All melting points are corrected.

bered that hydroquinones and quinones are generally sensitive to oxidation and to light, especially when damp or in solution. The dry crystals are stable in the refrigerator.

Reduction of Esters.—The general procedure is illustrated by the reduction of IIIa to IIa. A solution of 5.0 g (0.02 mole) of 2,5-dihydroxyterephthalic ethyl ester[9] in 50 ml of dry THF was added dropwise to a well-stirred slurry of 3.0 g (0.079 mole) of lithium aluminum hydride in 40 ml of dry THF. The mixture was then heated to reflux, with stirring, for 1 hr. It was cooled in an ice bath while the excess lithium aluminum hydride was destroyed by careful addition of 5 ml of cold water. Then 40 ml of 50% sulfuric acid and 40 ml of saturated ammonium chloride were added. Two layers formed. The upper THF layer was decanted and the lower was extracted with four 80-ml portions of THF. The combined THF layers were shaken with anhydrous magnesium sulfate, filtered, and concentrated *in vacuo* at room temperature to about 50 ml. During this process crystallization started; it was completed at −20° overnight. The product was filtered, washed with a small amount of THF, and dried *in vacuo*. The slightly brown material was purified by dissolving it in a minimum amount of dimethylformamide at room temperature and adding ten times its volume of ether. Crystallization started very slowly and yielded long, white needles, 2.5 g (75%). The material decomposes gradually on heating, thus preventing a determination of the melting point.

2,5-Bis(hydroxymethyl)hydroquinone (IIa) was prepared by reduction of IIIa: yield 75%.

Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.65; H, 6.10.

Oxidative titration with ceric ammonium nitrate in 90% acetic acid[1] gave 94.5% of the calculated value. The nmr spectrum from dimethyl sulfoxide showed single peaks at δ 4.50 and 6.81, relative intensity 2:1, and a very broad absorption at δ 6.3.

2,5-Bis(2′-hydroxyethyl)hydroquinone (IIc).—This was prepared in over-all yield of 76.5% by reduction of IIIb. It could be recrystallized from a small amount of hot water to give long white needles, mp 184°.

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.60; H, 7.12. Found: C, 60.40; H, 7.25.

The nmr spectrum in pyridine showed two triplets at δ 3.06 and 4.06. No other aliphatic protons could be detected. Oxidation with ceric ammonium nitrate in 90% acetic acid gave 97.3% of the calculated value.

2,5-Bis(3′-hydroxypropyl)hydroquinone (IIe).—White crystals, obtained from the reduction of IIIf were washed with hexane, and with acetonitrile. Recrystallization from a minimum amount of hot water gave 66% yield of pure white prisms, mp 168.5°.

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.57; H, 8.07.

The nmr examination in pyridine gave the signals for the aliphatic side-chain protons at δ 1.88 (m), 2.88 (m), and 3.66 (tr). Oxidative titration with ceric ammonium nitrate in 90% acetic gave 98.5% of the calculated value.

Acetylation of the Hydroquinonediols and Quinonediols.—As an example, to a slurry of 0.34 g (2.0 mmole) of 2,5-bis(hydroxymethyl)hydroquinone IIa in 10 ml of THF at 0° were added 2.0 ml of pyridine and 1.0 ml of acetyl chloride. The resulting mixture was heated 5 min on the steam bath then poured into 20 ml of ice water. The almost clear solution was filtered and extracted with two 10-ml portions of ether. The combined ether extracts, washed with water and dried over magnesium sulfate, yielded 61.5% of the desired tetraacetate. Recrystallization from a mixture of toluene and pentane yielded pure white crystals.

2,5-Bis(hydroxymethyl)hydroquinone Tetraacetate (IIb).—White crystals were obtained by acetylation of IIa: mp 115–116° (lit. 119–120°).[10]

Anal. Calcd for $C_{16}H_{18}O_8$: C, 56.80; H, 5.36. Found: C, 57.02; H, 5.18.

The nmr spectrum in $CDCl_3$ gave signals at δ 2.08 (s), 2.32 (s), 5.08 (s), and 7.27 (s).

2,5-Bis(2′-hydroxyethyl)hydroquinone tetraacetate (IId) was prepared by acetylation from IIc as white platelets, mp 80°, in 85% yield.

Anal. Calcd for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05. Found: C, 58.83; H, 6.09.

The nmr spectrum in $CDCl_3$ showed signals at δ 2.07 (s), 2.37 (s), 2.89 (m), 4.32 (tr), and 7.10 (s).

2,5-Bis(3′-hydroxypropyl)hydroquinone tetraacetate (IIf) was prepared by acetylation from IIc as white plates (from *n*-heptane), mp 78–80°, in 82% yield.

Anal. Calcd for $C_{20}H_{26}O_8$: C, 60.90; H, 6.64. Found: C, 60.19; H, 6.36.

The nmr spectrum in $CDCl_3$ showed signals at δ 1.96 (m), 2.05 (s), 2.34 (s), 2.55 (m), 4.15 (tr), and 7.03 (s).

2,5-Bis(acetoxymethyl)-1,4-benzoquinone (Id) was prepared by acetylation from Ia in 83% yield. Yellow, needlelike crystals, mp 134° were recrystallized from *n*-heptane containing about 40% toluene.

Anal. Calcd for $C_{12}H_{12}O_6$: C, 57.14; H, 4.80. Found: C, 57.21; H, 4.69.

The nmr spectrum in $CDCl_3$ showed signals at δ 2.20 (s), 5.09 (d), and 6.79 (tr).

2,5-Bis(2′-acetoxyethyl)-1,4-benzoquinone (Ie) was prepared by acetylation from Ib as yellow platelets, mp 87°, in 95% yield and was recrystallized from boiling *n*-heptane.

Anal. Calcd for $C_{14}H_{16}O_6$: C, 60.00; H, 5.75. Found: C, 59.89; H, 5.83.

The nmr spectrum in $CDCl_3$ showed signals at δ 2.08 (s), 2.80 (m), 4.35 (tr), and 6.76 (tr).

2,5-Bis(3′-acetoxypropyl)-1,4-benzoquinone (If) was prepared from Ic by acetylation, as bright yellow platelets, mp 57°, in 92.5% yield and was recrystallized from boiling *n*-heptane.

Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 61.46; H, 6.42.

The nmr spectrum in $CDCl_3$ showed signals at δ 1.95 (m), 2.10 (s), 2.53 (m), 4.20 (tr), and 6.70 (tr).

Oxidation of the Substituted Hydroquinones with Silver Oxide.—As an example, 0.34 g (2.0 mmole) of IIa, in 40 ml of dry THF was treated with 0.6 g of silver oxide and 1.0 g of magnesium sulfate. The mixture was stirred for 30 min at room temperature and then filtered. The yellow filtrate, upon evaporation *in vacuo* at room temperature, gave a yellow, crystalline mass. This was dissolved in a small amount of acetone at room temperature. Upon adding five times the volume of *n*-pentane, 0.31 g (92.5) of bright yellow crystals were obtained: mp 134–135° (lit.[10] 139°).

2,5-Bis(hydroxymethyl)-1,4-benzoquinone (Ia) was prepared, by oxidation of IIa, as yellow crystals.

Anal. Calcd for $C_8H_8O_4$: C, 57.14; H, 4.80. Found: C, 57.32; H, 4.91.

The nmr spectrum in acetonitrile showed signals at δ 4.40 (qu) and 6.67 (tr).

2,6-Bis(formyl)-4-methoxyphenol (VI). Attempted Preparation of 2,6-Bis(hydroxymethyl)quinone (IV).—A mixture of 4.6 g (0.025 mole) of 2,6-bis(hydroxymethyl)-4-methoxyphenol (V)[11] and 10 g of silver oxide in 150 ml of dry THF was refluxed with stirring for 45 min. Filtration and removal of the solvent *in vacuo* at room temperature left a yellow, crystalline mass. This was washed with ether and recrystallized from hot ethyl acetate to yield 1.5 g of very pure VI, mp 137° (lit.[10] 138°). Working up the residues raised the over-all yield to 44.5%. The product in $CDCl_3$ showed four single nmr signals at δ 3.88, 7.51, 10.22, and 11.12. The dioxime melted at 190° (lit.[10] 190°). No other product could be isolated from the reaction mixture described above.

2,5-Bis(2′-hydroxyethyl)-1,4-benzoquinone (Ib) was prepared by oxidation of IIc. The yellow, crystalline product was recrystallized from THF–pentane to give yellow needles, mp 77° in 95% yield.

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.17. Found: C, 61.19; H, 6.32.

The nmr spectrum in $CDCl_3$ showed signals at δ 2.12 (d) 2.67 (m), 4.82 (tr), and 6.71 (tr).

2,5-Bis(3′-hydroxypropyl)-1,4-benzoquinone (Ic).—This was prepared by oxidation of IIe. On recrystallization from THF and pentane, it gave 93% yield of bright yellow needles, mp 99°.

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.58; H, 7.47.

The nmr spectrum from $CDCl_3$ showed signals at δ 1.72 (m), 1.92 (d), 2.52 (m), 3.65 (tr), and 6.57 (tr).

Esterification of Compound IIIc.—The usual esterification procedure, adding 5.0 g (0.021 mole) of IIIc to 30 ml of methanol containing 1 ml of concentrated sulfuric acid with stirring until a clear solution formed (*ca.* 5 min) and the ester crystallized, yielded, on work-up and recrystallization from a large amount of boiling THF, white crystals, mp 212° (89.5%).

Anal. Calcd for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55. Found: C, 56.52; H, 5.68.

The nmr spectrum in pyridine gave two singlets in the ratio 2:3 at δ 3.74 and 3.37.

1,4-Dimethoxy-2,5-bis(2′2′-dicarbethoxyethyl)benzene (VIII) was prepared in 83% yield as long white needles, mp 104°, by a standard malonic ester synthesis applied to 2,5-bis(chloromethyl)-1,4-dimethoxybenzene.[14]

Anal. Calcd for $C_{24}H_{34}O_{10}$: C, 59.74; H, 7.25. Found: C, 59.63; H, 7.15.

The nmr spectrum from CCl_4 showed signals at δ 1.21 (tr), 3.12 (d), 3.64 (tr), 3.90 (s), 4.19 (qu), and 6.74 (s).

Hydroquinone-2,5-bis(ethyl-2′-carboxylic acid) (IIIe).—The malonic ester derivative VIII was demethylated at the methoxyl groups, and hydrolyzed and decarboxylated in one step by heating with 48% hydrobromic acid. Up to a bath temperature of 120°, ethyl bromide distilled. The temperature was raised to 140° until decarboxylation (foaming) of the mixture was completed. Finally, the temperature was raised to 160°, and maintained for 4 hr to complete the demethylation. Work-up of the product (it crystallized from the solution upon cooling in an ice bath) and recrystallization from a minimum amount of boiling water gave a 90% yield of nearly pure IIIe. Recrystallization from THF–heptane gave small white needles, mp 290°.

Anal. Calcd for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55. Found: C, 56.71; H, 5.70.

2,5-Bis(2′-carbethoxyethyl)hydroquinone (IIIf).—The diacid IIIe was esterified in absolute ethanol in the usual manner, with recrystallization of the product in the minimum amount of hot ethanol that was ~20% water. A 91% yield of white needles, mp 114°, was obtained.

Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.85; H, 7.10.

The nmr spectrum in acetonitrile gave signals at δ 1.21 (tr), a multiplet centered at 2.6, 4.18 (qu), 6.65 (s), and a broader absorption at 6.78.

Oxidation of Esters.—The hydroquinone diacid ester (XIIIa, XIIIb, XIIIc) in the amount of 8.0 mole equiv was dissolved in 40 ml of 95% ethanol. This solution was slowly poured into a solution of 2.9 g (18 mole equiv) of ferric chloride in 60 ml of 90% ethanol. The mixture was heated for 5 min on a steam bath, allowed to cool for about 10 min and poured into 70 ml of ice water. The resulting deep yellow solution was extracted once with chloroform. The chloroform extract, on drying over magnesium sulfate, filtration, and evaporation *in vacuo*, yielded yellow, crystalline material which could be recrystallized from boiling heptane containing a small amount of toluene.

2,5-Bis(carbethoxymethyl)-1,4-benzoquinone (XIIIa) was obtained as yellow needles, mp 86–87°, yield 88%.

Anal. Calcd for $C_{14}H_{16}O_6$: C, 60.00; H, 5.75. Found: C, 60.07; H, 5.51.

The nmr spectrum in $CDCl_3$ showed signals at δ 1.28 (tr), 3.49 (d), 4.21 (qu), 6.82 (tr).

2,5-Bis(carbomethoxymethyl)-1,4-benzoquinone (XIIIb) was obtained as pale yellow crystals, mp 120°, yield 71%.

Anal. Calcd for $C_{12}H_{12}O_6$: C, 57.14; H, 4.80. Found: C, 56.93; H, 5.06.

The nmr spectrum from $CDCl_3$ showed signals at δ 3.46 (d), 3.71 (s), and 6.78 (tr).

2,5-Bis(2′-carbethoxyethyl)-1,4-benzoquinone (XIIIc) was obtained as bright yellow plates, mp 56–57°, yield 92%.

Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.11; H, 6.52.

The nmr spectrum from $CDCl_3$ showed signals at δ 1.27 (tr), 2.69 (m), 4.19 (qu), and 6.65 (tr).

Phenylurethane Preparation.—As a model reaction, 2,5-bis-(3′-hydroxypropyl)-1,4-benzoquinone (0.22 g, 1.0 mmole) was dissolved in 6.0 ml of dry THF. After addition of 1.0 ml of phenyl isocyanate and 2 drops of triethylamine, the mixture was warmed on the water bath to 60° for 5 min, and 20 ml of *n*-pentane was added. Upon cooling, yellow crystals separated. These could be recrystallized from boiling ethanol. A yield of 69% of fine yellow needles was obtained, mp 158°. A sample twice recrystallized from methanol gave the following analysis.

Anal. Calcd for $C_{26}H_{26}N_2O_6$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.27; H, 5.54; N, 5.87.

The nmr spectrum in $CDCl_3$ showed signals at δ 1.95 (m), 2.51 (m), 3.51 (s), 4.24 (tr), 6.60 (tr), and 7.35 (m).

Polyester from 2,5-(2′-Hydroxyethyl)-1,4-benzoquinone (Ib) and Sebacoyl Chloride.—To a solution of freshly prepared and well-drained quinonediol Ib, exactly 196.12 mg by weight (1.0 mmole) in 2 ml of THF, was added exactly 239.14 mg of freshly distilled sebacoyl chloride in 5.0 ml of dry THF. The mixture was kept at 0° while 1.0 ml of pyridine was added. It was stirred well and allowed to come to room temperature. Soon after the addition of pyridine, white pyridine hydrochloride began to precipitate. After 1 hr at room temperature the mixture was filtered and the filtrate poured into ten times its volume of *n*-pentane. The polyester precipitated as brown flakes which formed a light brown, waxy mass. Two precipitations from solution in THF by pouring into an excess of *n*-pentane gave a product (the infrared spectrum and viscosity were discussed above) that was soluble in THF, dioxane, and dimethylformamide and insoluble in water, alcohol, and petroleum ether.

Polyester from 2,5-Bis(2′-hydroxyethyl)-1,4-benzoquinone (Ib) and Terephthaloyl Dichloride.—Exactly 196.12 mg (1.0 mmole) of freshly prepared and well-dried quinonediol Ib and exactly 203.03 mg (1.0 mmole) of terephthaloyl dichloride were dissolved in 4.0 ml of dry THF. At 0° 1 ml of pyridine was added and the mixture was warmed to 30° for 10 min. The viscous yellow liquid that formed was decanted from a white precipitate of pyridine hydrochloride into 30 ml of cold water. Yellow flakes precipitated which yielded yellow powder after filtration and washing with water. It was insoluble in most organic solvents, and soluble only in hot dimethylformamide or dimethyl sulfoxide. For further examination (the infrared spectrum was reported above) it was dissolved in hot dimethylformamide and reprecipitated by pouring into water.

Polyester from Hydroquinone-2,5-bis(methylene carboxylic Acid) (IIIc) and 1,4-Butanediol.—Exactly 452.38 mg (2.0 mmoles) of very pure hydroquinone-2,5-diacetic acid (IIIc),[13] and 180.24 mg (2.0 mmoles) of freshly distilled 1,4-butanediol were suspended in 10 ml of freshly distilled toluene. To this was added 2.0 mg of *p*-toluenesulfonic acid and 2.0 mg of antimonous oxide.[16] The mixture was heated to the boiling point of toluene under a slow stream of nitrogen. During 3 hr toluene was slowly distilled off while fresh xylene was slowly added. The bath temperature was raised to 150° until all the xylene was removed. The residue was cooled and washed with methanol. It was dissolved in 5 ml of dimethylformamide and filtered through glass into 50 ml of cold water. The polyester precipitated as a white powder. It was dried *in vacuo* to yield a brittle, slightly yellow material insoluble in THF, alcohols, water, and petroleum ether and soluble in the cold only in dimethylformamide. The yield was 52%. The infrared spectrum and viscosity were reported above.

Polyurethane from 2,5-Bis(3′-hydroxypropyl)-1,4-benzoquinone (Ic) and Methylenebis(*p*-phenyl isocyanate).—Exactly 224.26 mg (1.0 mmole) of the freshly prepared quinonediol Ic and exactly 250.26 mg (1.0 mmole) of the diisocyanate were dissolved in 10 ml of dry THF. One drop of triethylamine was added. The mixture was kept for 3 hr at 30°. The very viscous solution was poured into 100 ml of *n*-pentane, whereupon yellow flakes of the polymer precipitated. The polymer was twice reprecipitated from THF–*n*-pentane. The polymer was soluble in THF, dioxane, and dimethylformamide and insoluble in alcohols, water, and petroleum ether. The infrared spectrum and viscosity were reported above.

Registry No.—Ia, 13949-75-2; Ib, 13949-76-3; Ic, 13949-77-4; Id, 13949-78-5; Ie, 13949-79-6; If, 13949-80-9; IIa, 13949-81-0; IIc, 13949-82-1; IId, 13949-83-2; IIe, 13949-84-3; IIf, 13949-85-4; IIIc, 13949-86-5; IIIe, 13949-87-6; IIIf, 13949-88-7; VIII, 13949-89-8; XIIIa, 5628-31-9; XIIIb, 13949-91-2; XIIIc, 14053-41-9; phenylurethan ($C_{26}H_{26}N_2O_6$), 13949-92-3.

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