Electron-Transfer Polymers. XXXV. Inductive Effects of Substituents upon Spectral and Redox Properties of *p*-Benzoquinones

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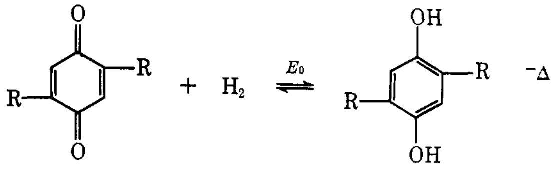
The differences in free-energy change in a series of monosubstituted and of 2,5-disubstituted 1,4-benzoquinones relative to respective reference compounds, ethyl-*p*-benzoquinone and 2,5-dimethyl-1,4-benzoquinone, are correlated with inductive electron-withdrawing effects of the polar substituents upon the position of the *p*-benzoquinone–hydroquinone equilibrium. The effect is correlated to an increase in the ir frequencies of C=C and C=O stretch. The closer the polar group to the ring the greater the effect, giving a fairly clear linear relation between frequencies and standard potentials. The orders of magnitude of the differences in free energy between substituted and reference compounds are comparable to and in the same direction as the changes produced by these substituents upon the free energy of dissociation of acetic acid—the classical case of inductive influence. It is shown with substituents that include hydroquinonyl and *p*-benzoquinonyl as the polar groups that the inductive effect of the polar group falls off with distance and reaches zero when a linear chain of about five CH_2– groups separates polar group and ring. These data thus provide a frame of reference for judging and predicting the behavior of redox polymers related to these models. It seems that the main contribution to the interaction between neighboring redox units is communicated through induction and not through internal charge transfer.

Although many different types of redox polymers have been synthesized during the last twenty years, their redox behavior is still not well understood. This report presents and discusses the properties of new 2,5-disubstituted 1,4-benzoquinones[2a] (*p*-benzoquinones) from which new types of redox polymers have been prepared[2b] and of some hydroquinone dimers. That inductive effects exist, wherein an increase in the number of CH_2 groups inserted between a substituent group and a functional group attenuates in a regular way the effect of the one upon the other, is well known.[3] We present such correlations to redox and spectral properties of *p*-benzoquinones that are new, as far as we can determine. These substituted *p*-benzoquinones serve as models. From their behavior one is able to extrapolate to polymer behavior. If polymers related to these models show behavior not observed with the low molecular weight models, the departure may with firmer reason be discussed as "polymer effect."

The results of redox titrations for different 2,5-disubstituted benzoquinones are listed in Table I.

The titrations were carried out in 90% acetic acid with ceric ammonium nitrate $[Ce(NH_4)_2(NO_3)_6]$ in the same solvent as oxidant. From the observed potentials the standard potentials (pH 0, 25°) in Table I were calculated. To bring out effects of substituents, 2,5-dimethyl-1,4-benzoquinone (*p*-xyloquinone) was chosen as reference compound. The difference in potential between this reference compound and the particular substituted quinone is reported in column 5 of Table I. For a given functional group, this difference is greatest when the polar substituent is separated by only one —CH_2— group from the ring. It becomes smaller as more —CH_2— groups separate it from the ring. From the standard potential, ΔG_Q, the change in free energy that takes place in the particular redox reaction is calculated. Again in reference to 2,5-dimethyl-1,4-benzoquinone, the difference in free-energy changes, $\Delta(\Delta G_Q)$, can be calculated. These are shown in column 6 of Table I. For example, from the increase in standard potential of 2,5-bishydroxymethyl-1,4-benzoquinone over the reference compound, it is concluded that it is easier by 1.6 kcal/mol to reduce the hydroxymethyl-substituted compound than the methyl-substituted compound. As the distance of the polar group from the ring is increased, the difference in free-energy change $\Delta(\Delta G_Q)$ approaches zero. The same effect is observed with monosubstituted 1,4-benzoquinones. The relevant quantities for some monosubstituted quinones are presented in Table II, where ethyl-1,4-benzoquinone is used as the reference. Many of the differences in free energy change for the monosubstituted compounds are close to half of those for the disubstituted.

In the following reaction (eq 1) a major part of the driving force is certainly the gain in resonance energy of



$-\Delta G$ (1)

the aromatic hydroquinone over the quinone.[4] Other factors, such as inductive effects, hydrogen bonding, charge-transfer interactions, and solvent effects, will enhance, or oppose, this driving force. It is the total free-energy change that determines the potential. In these quinones, the polar groups in the side chains are connected through σ bonds only to the reaction center (the ring system); hence resonance interactions must be excluded. Careful investigations of nmr and ir spectra of the quinonediols, quinone diacids, and hydroquinone esters gave in most cases no evidence of intramolecular hydrogen bonding.[5] No indication for unusual charge-transfer interactions could be found; thus, these two interactions can only have minor effects, insufficient to explain the observed changes. The remaining possibility is inductive effect. Since all titrations were done at pH 0, while the first acid dissociation constant of hydroquinone is above 7, it

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(2) (a) G. Wegner, N. Nakabayashi, and H. G. Cassidy, *J. Org. Chem.*, **32**, 3155 (1967); (b) *J. Polym. Sci., Part B-6*, 97 (1968).

(3) For example, see R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956.

(4) M. G. Evans and J. De Heer, *Chem. Soc. Quart. Rev.*, **4**, 94 (1950).

(5) Unpublished work of T. F. Keyes, III.

TABLE I

INFLUENCE OF THE INDUCTIVE EFFECT ON REDOX POTENTIAL AND SPECTRA OF 2,5-DISUBSTITUTED 1,4-BENZOQUINONES

Figure 1 no.	Substituents R (in eq 1)	Registry no.	E_0, mV	ΔE,[a] mV	$\Delta(\Delta G_Q)$[b] kcal	Ir frequencies,[c] cm^{-1} C=O	C=C	Chemical shift,[d] τ
1	$—CH_3$	137-18-8	602	...	...	1643 (1667)	1620	
2	$—CH_2OH$	13949-75-2	636	34	1.57	1653	1621	3.33
3	$—(CH_2)_2OH$	13949-76-3	620	18	0.83	1656	1611	3.29
4	$—(CH_2)_3OH$	13949-77-4	607	5	0.23	1655	1610	3.43
5	$—(CH_2)_2OCOCH_3$	13949-79-6	635	33	1.54	1660	1618	3.24
6	$—(CH_2)_3OCOCH_3$	13949-80-9	616	14	0.65	1658	1615	3.30
7	$—CH_2—CO_2H$	20452-46-4	655	53	2.45	1665	1625	
8	$—(CH_2)_2CO_2H$	16076-07-6	629	27	1.29	1660	1614	
9	$—CH_2CO_2C_2H_5$	5628-31-9	664	62	2.86	1667	1622	3.18
10	$—(CH_2)_2CO_2C_2H_5$	14053-41-9	623	21	0.97	1658	1611	3.35
	$—H$		706	...	...	1659, 1663	1593	

[a] $\Delta E = E_0$ of substituted quinone $-$ E_0 of 2,5-dimethyl-1,4-benzoquinone. [b] See text for explanation. [c] Compounds were dissolved in tetrahydrofuran. [d] Compounds were dissolved in deuteriochloroform.

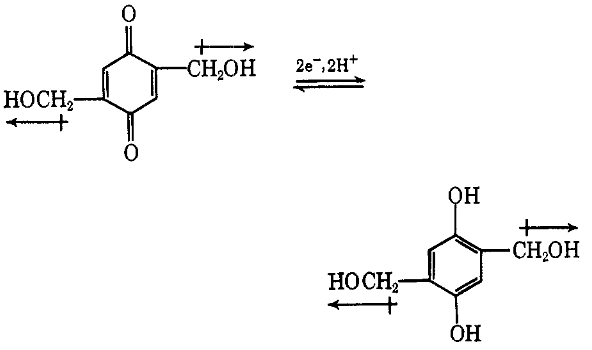
TABLE II

INFLUENCE OF THE INDUCTIVE EFFECT ON REDOX POTENTIAL AND SPECTRA OF MONOSUBSTITUTED BENZOQUINONES

Substituent R	E_0, mV	ΔE,[a] mV	$\Delta(\Delta G_Q)$,[b] kcal	Ir frequencies,[c] cm^{-1} C=O	C=C
$—CH_2—CH_3$	652	..	...	1663	1598
$—(CH_2)_2OH$	669	17	0.78	1663	1601
$—CH_2—CO_2H$	680	28	1.29	1665	1603
$—(CH_2)_2CO_2H$	666	14	0.65	1664	1601
$—CH_2—CO_2C_2H_5$	678	26	1.20	1664	1602
$—(CH_2)_2CO_2C_2H_5$	665	13	0.60	1664	1603

[a-c] See footnotes *a–c* of Table I.

must be that in every case the reduced forms are un-ionized and therefore comparable. That is, no account need be taken of degrees of ionization due to the substituent.



(2)

In eq 2, a polar group contributes to a permanent dipole, oriented as shown. This influences the charge distribution on the ring in the direction shown (*i.e.*, with the positive pole closer to the ring). In these circumstances, the frequencies of vibration of the —C=C— stretch and —C=O double bond of the quinones should be increased, the more so the closer the polar group to the ring. In Table I, columns 7 and 8, these effects are clearly seen. Further, if the frequencies are plotted against the observed standard potentials, fairly clear straight-line relations are obtained identical in slope within the limits of the measurements. These results recall the correlations found by Goulden[6] between O—H stretching frequencies and pK_a values of carboxylic acids and phenols, and the inductive effects described by Bellamy.[7] An influence of the substituent on the chemical shift of the ethylenic proton due to the substituent is also found, as shown in the last column of Table I.

In the monosubstituted *p*-benzoquinones in solution (Table II) there is only one C=O and one C=C vibration, suggesting that the vibration of the substituted double bond is linked to that of the unsubstituted double bond. The influence of the substituent is not very marked, which suggests that the effect is diluted out by this linkage. A similar supposition applies to the carbonyl absorption for monosubstituted *p*-benzoquinones.

A more important test of the existence of an inductive effect may be made by comparing the effect of a given substituent upon the redox potential with that produced by a substituent on the pK_a value of a carboxylic acid. This comparison invokes the classical example of inductive influence[8] and applies it in this new situation. The comparison is made in Table III. Acetic acid serves as the reference compound for the other carboxylic acids, with the di- and monosubstitued reference compounds as before (Tables I and II). Again the comparison is made in the form of differences in free-energy changes, $\Delta(\Delta G)$. The orders of magnitude are comparable, and the changes occur in the same directions. When, for example, the $—CH_3$ group of acetic acid is replaced by $—CH_2OH$, the free energy of dissociation increases by 1.28 kcal/mol. The corresponding replacement in 2,5-substituted 1,4-quinones raises the free energy of the redox reaction by 1.57 kcal/mol. It may be supposed, in view of the many factors that contribute to the free-energy change in a redox reaction,[4] that the good agreement between columns 3 and 4 of Table III is fortuitous; however, the consistent directions of change, and the similar orders of magnitude of the changes, are probably meaningful. When there is only one substituent present in the redox system, the influence on the free-energy change is less, and in some cases close to half that for the disubstituted compounds. (It must be pointed out that these data are not adequate to allow a decision as to whether ΔG of electron transfer is or is not predominant over ΔG of proton transfer in the oxidation or reduction of these substances.)

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(6) J. D. S. Goulden, *Spectrochim. Acta*, **6**, 129 (1954).

(7) L. J. Bellamy, *J. Chem. Soc.*, 4221 (1955). Bellamy refers to earlier literature. See also Taft, ref 3.

(8) A. Eucken, *Angew. Chem.*, **45**, 203 (1932); E. A. Braude and F. C. Nachod, Ed., "Determination of Organic Structures by Physical Methods," Vol. I, Academic Press, New York, N. Y., 1955.

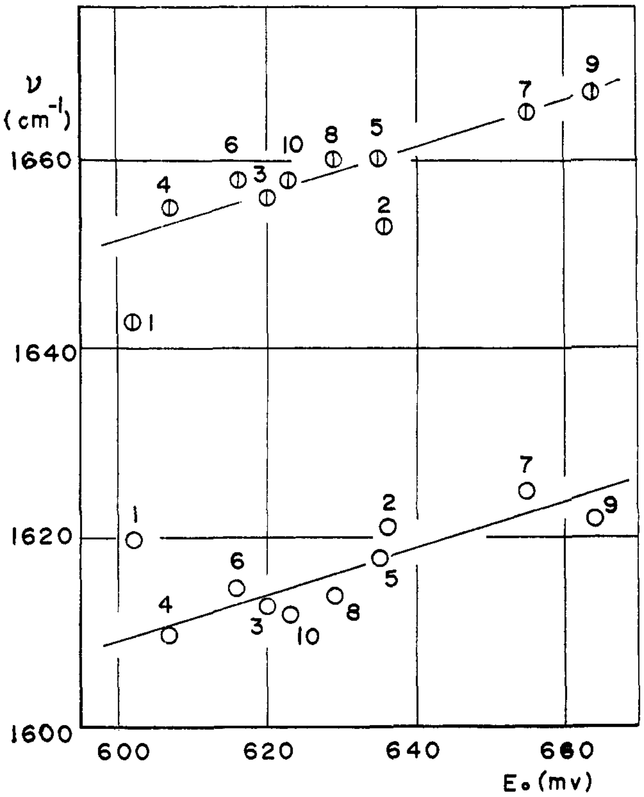


Figure 1.—Plot of ir frequencies of C=O (⦶) and C=C (O) stretching against observed standard potentials of 2,5-disubstituted benzoquinones. Key to the numbers is found in Table I.

Table III

Comparison of the Influence of the Inductive Effect in Substituted *p*-Benzoquinones and Substituted Carboxylic Acids, R—COOH

	Carboxylic acids		*p*-Benzoquinones	
			2,5-disubstd,	Monosubst,
Substituent R	pK_a[a]	$\Delta(\Delta G_a)$,[b] kcal	$\Delta(\Delta G_Q)$,[c] kcal	$\Delta(\Delta G_Q)$,[d] kcal
CH_3—	4.76	...	...	...
HO_2C—CH_2—	2.83	2.63	2.45	1.29
$C_2H_5OCOCH_2$—	3.35	1.92	2.86	1.20
$HOCH_2$—	3.83	1.28	1.57	
$HO_2C(CH_2)_2$—	4.19	0.78	1.29	0.65
$C_2H_5OCO(CH_2)_2$—	4.52	0.33	0.97	0.60
$HO(CH_2)_2$—	4.51	0.34	0.83	0.78
$HO(CH_2)_3$—	4.72	0.05	0.23	
C_6H_5—CH_2—	4.31	0.61		0.55[e]
C_6H_5—$(CH_2)_2$—	4.66	0.14		0.37[e]

[a] Values taken from ref 8. [b] Difference in free-energy change of dissociation between the substituted acid and acetic acid. [c] See Table I. [d] See Table II. [e] Values taken from ref 13.

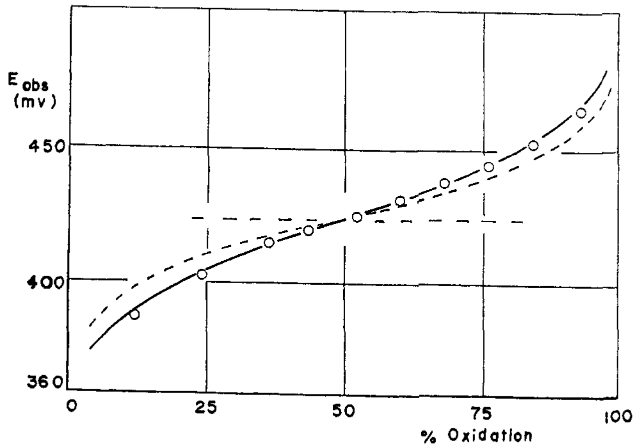
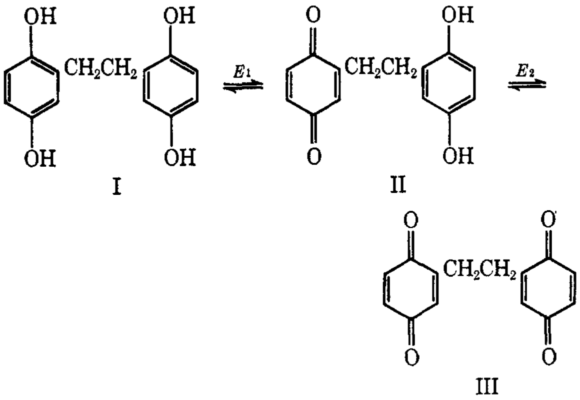


Figure 2.—The solid line connects observed potentials in the oxidative titration of 1,2-(2′,5′-dihydroxyphenyl)ethane. The dashed line is that of a theoretical two-electron oxidation with the same midpoint potential.

In applying these findings to the behavior of oligomers, there are cases wherein hydroquinonyl or quinonyl groups are the polar substituents on side chains to other such groups. Extending a series already begun by Moser and Cassidy,[9] 1,2-bis(2′,5′-dihydroxyphenyl)ethane (I) was prepared. The solid line in Figure 2 shows the oxidative titration curve for this compound; the dashed line is that of a theoretical two-electron oxidation with the same midpoint potential. The index potential of the dimer curve is 19 mV instead of the theoretical 14 mV. This implies that more than one species is being titrated. These species are shown in eq 3 and 4. The redox potentials E_1 and E_2 can be calculated from the slope of the curve or from the index potentials; and the intermediate-formation constant K can be calculated.[10,11]



(3)

$$\mathrm{I} + \mathrm{III} \overset{K}{\rightleftharpoons} 2\,\mathrm{II} \qquad (4)$$

Examination of the dimers already prepared by Moser[9] disclosed similar behavior. These data are gathered in Table IV, where it is evident that, when the connecting bridge contains 5 —CH_2— groups, the two rings behave independently of each other. Thus, a bridge longer than about 5 —CH_2— units effectively isolates the redox groups by this criterion. This is supported (Table IV) with an oligomer SD-3 in which the redox units (about nine of them) are each separated from the other by a long bridge containing ester and ether links. The titration curve for this oligomer is ideal, with an index potential of 14 mV.[12] There is evidence, however, that these conclusions from monomers and oligomers must not be extrapolated indiscriminately to polymers.

Finally, with these dimers it becomes possible to compare the differences in free-energy changes $\Delta(\Delta G_Q)$ for a series of compounds in which a *p*-benzoquinone has, within the same distance, either a hydroquinone

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(9) R. E. Moser and H. G. Cassidy, *J. Org. Chem.*, **30**, 2602 (1965).

(10) G. Manecke and H.-J. Förster, *Makromol. Chem.*, **52**, 147 (1962).

(11) B. Elema, *J. Biol. Chem.*, **100**, 149 (1933).

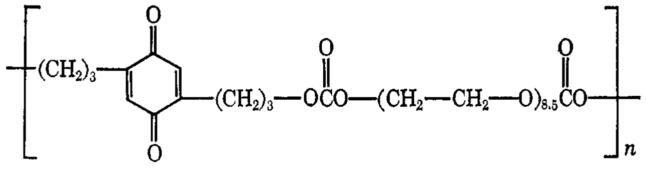
(12) G. Wegner, N. Nakabayashi, S. Duncan, and H. G. Cassidy, *J. Polym. Sci., Part A-1*, **6**, 3395 (1968).

TABLE IV

RESULTS OF REDOX TITRATIONS OF VARIOUS OLIGOMERIC *p*-BENZOQUINONES

Bridge R	E_m, mV	E_i, mV	K	$E_2 - E_1$, mV	E_1, mV	E_2, mV
—$(CH_2)_2$—	652	19	12.8	33	636	669
—$(CH_2)_3$—	652	17.5	9.1	28	638	667
—$(CH_2)_5$—	655	14.0	0	0	655	655
SD-3[a]	616	14.0	0	0	616	616

[a] SD-3 is an oligomer of the structure which appears below.



where $n \approx 9$

E_m is the midpoint potential, E_i the index potential, and K is the intermediate formation constant.

or a *p*-benzoquinone group. This comparison is made in Table V. The values for the methylene-bridged dimer are from Manecke.[13] Again, $\Delta(\Delta G_Q)$ decreases with distance between the neighboring groups, falling to zero when the bridge reaches 5 —CH_2— groups. This pattern, and the orders of magnitude of the effects when the bridges are short, supports the inference that the effect is inductive. This conclusion is further supported when the influence of hydroquinone and *p*-benzoquinone substituents upon the pK_a values of the substituted carboxylic acids is examined, as shown in the last two columns of Table V. The influence of these groups on the free energy of dissociation of the acids is about half that for the redox reaction. Possibly the reason for this is that a relatively large *p*-benzoquinone or hydroquinone group with many internal dipoles may interact to a greater extent with a group of the same size than with a small carboxylic acid group. It seems, in summary, that the main contribution to interaction between neighboring redox units is communicated through induction. Other contributions to the total free-energy change, such as stabilization through internal charge transfer[14] or homoconjugation of adjacent rings,[15] cannot be excluded, but appear to be of minor importance.

Experimental Section

Spectra.—Infrared spectra were obtained with a Perkin-Elmer Model 421 spectrometer. Tetrahydrofuran for infrared measurements was carefully purified and distilled immediately before use. The solutions of the quinones to be measured were about 2% by weight. Ultraviolet spectra were measured with a Bausch & Lomb Spectronic 505 spectrometer.

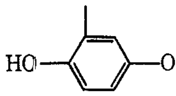
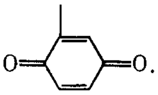
Titrations.—The apparatus used was that described elsewhere.[16,17] Potentials were determined by means of a Leeds and Northrup Speedomax recording potentiometer. The titrations were carried out in a thermostatically controlled water bath at 25°. All reagents were transferred, and titrations were carried out under the usual precautions.[17] Potentials were measured against a saturated calomel electrode which had been calibrated on the hydrogen scale. Thus all potentials are reported on the hydrogen scale and have been calculated to pH 0. The calculations neglect effects of ionization or salt error. Ceric ammonium nitrate, $Ce(NH_4)_2(NO_3)_6$, was used as oxidizing agent and was dissolved in the same solvent as was the hydroquinone being titrated (90% acetic acid, v/v). In a typical run, about 0.1 mmol of a hydroquinone was dissolved in 100 ml of solvent. The end point of titration was reached with about 3.0 ml of the titrant added. During titration, the change in pH was less than 0.1 pH unit (measured with a glass electrode) and was neglected in calculations. The final values for the standard potentials were determined as the middle of several runs. They are exact to ± 2 mV. pK_a values were determined potentiometrically by means of a Leeds and Northrop pH meter. The value of ΔG is good to within 0.1 unit.

TABLE V

INFLUENCE OF A *p*-BENZOQUINONE OR HYDROQUINONE AS SUBSTITUENT ON THE REDOX POTENTIAL OF A SECOND *p*-BENZOQUINONE OR ON THE pK_a VALUE OF A CARBOXYLIC ACID, R—COOH

	p-Benzoquinones		Carboxylic acids	
Substituent R[c]	E_0, mV	$\Delta(\Delta G_Q)$,[a] kcal	pK_a	$\Delta(\Delta G_a)$,[b] kcal
HQ—CH_2—	647	$1.87^{15°}$	$4.14^{23°}$	0.89
Q—CH_2—	687		$3.49^{23°}$	
HQ—$(CH_2)_2$—	636		4.49	
		1.52		0.53
Q—$(CH_2)_2$—	669		4.10	
HQ—$(CH_2)_3$—	638			
		1.29		
Q—$(CH_2)_3$	667			
HQ—$(CH_2)_5$—	655			
		0		
Q—$(CH_2)_5$—	655			

[a] $\Delta(\Delta G_Q)$ = difference in free-energy change for oxidation of a hydroquinone with hydroquinone as neighbor and with quinone as neighbor. [b] $\Delta(\Delta G_a)$ was calculated analogously to $\Delta(\Delta G_Q)$.

[c] HQ — =  ; Q — = .

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

2′-Hydroxyethyl-2,5-benzoquinone.—2′-Hydroxyethylhydroquinone[18] [0.31 g (2.0 mmol)]in 40 ml of dry ethyl ether 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 gave a yellow crystalline mass upon evaporation of the solvent *in vacuo*. It was recrystallized from normal heptane to give bright yellow needles, mp 36°; 86% yield. Upon reduction with sodium hydrosulfite the starting material was retrieved: ir 1651 (C=O), 1600 (C=C), 3340, 1300, 1050 (CH_2OH) cm^{-1}; nmr τ 3.23 (m), 6.15 (t), 7.31 (m), and 7.93 ppm (d).[19]

1,4-Dimethoxy-2-(2′,2′-dicarbethoxyethyl)benzene (IV).—This substance was prepared from 1,4-dimethoxy-3-chloromethylbenzene by a standard malonic ester synthesis as a colorless liquid, bp 157–160° (0.5 mm); yield, 70%; nmr τ 3.38 (s), 5.92 (qu), 6.26 (s), 6.32 (t), 6.33 (s), 6.42 (d), 8.84 (t).[19]

1,4-Dihydroxy-2(3′-propanoic acid)benzene (V).—Compound IV was refluxed for 4 hr with 48% hydrogen bromide. The hot solution was filtered, diluted with an equal amount of ice, and immediately extracted with several portions of ether. The

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[13] G. Manecke and D. Zerpner, *Makromol. Chem.*, **108**, 198 (1967).

[14] R. E. Moser, Dissertation, Yale University, 1965.

[15] S. E. Hunt, A. S. Lindsey, and N. G. Saville, *J. Chem. Soc.*, *B*, 791 (1967).

[16] I. D. Robinson, M. Fernandez-Refojo, and H. G. Cassidy, *J. Polym. Sci.*, **39**, 47 (1959).

[17] K. Kun and H. G. Cassidy, "Oxidation–Reduction Polymers (Redox Polymers)," Interscience Publishers, Inc., New York, N. Y., 1965.

[18] R. Stern, J. English, Jr., and H. G. Cassidy, *J. Amer. Chem. Soc.*, **79**, 5797 (1957).

[19] Elementary microanalyses were carried out by Galbraith Analytical Laboratories. Infrared data in the experimental part were obtained with the substances dissolved in KBr. Nmr data were obtained with a Varian Associates Model A-60 spectrometer. Chemical shifts were given in τ values. The letters in parentheses mean s, singlet; d, doublet; t, triplet; qu, quadruplet; m, multiplet. Analytical grade deuteriochloroform was used as solvent. All melting points are corrected.

combined ether extracts were washed with concentrated sodium chloride solution and dried over magnesium sulfate. Evaporation of the ether gave a brownish crystalline mass. Recrystallization from hot water gave thin white plates, mp 119–120°; yield 40%; ir 1705 (C=O), 1650 (COOH hydrogen bonded), 3380, 3250, 1395, 1190 (OH), 1595, 1500, 1455 (aromatic ring) cm^{-1}.

1,4-Dihydroxy-2-(2′-carbethoxyethyl)benzene.—Compound V was converted to the ethyl ester in anhydrous ethanol with hydrogen chloride gas as catalyst. Recrystallization from toluene–hexane gave small white needles, mp 78–79°; yield, 78%; ir 3350, 1370 (OH), 1610, 1525, 1450 (aromatic ring), 1700, 1200 (ester) cm^{-1}; nmr 3.10 (s), 3.35 (m), 4.14 (s), 5.85 (qu), 7.25 (m), and 8.78 ppm (t).[19]

Oxidation of Hydroquinone Acids and Esters. General Method.—The same general method was used as already reported,[2a] using ferric chloride as oxidizing agent in an ethanol–water mixture.

1,4-Benzoquinone-2,5-bis(3′-propanoic acid).—Recrystallization from tetrahydrofuran by addition of heptane gave yellow needles, mp 191–193°; yield 86%; ir 1710, 1228 (COOH), 1655, 1620 (quinone) cm^{-1}.

Anal. Calcd for $C_{12}H_{12}O_6$: C, 57.14; H, 4.80. Found: C, 57.25; H, 4.45.

1,4-Benzoquinone-2-(3′-propanoic acid) was obtained as small, dark yellow needles from hexane–tetrahydrofuran, mp 137–139°; yield 72%; ir 1710, 1210 (COOH), 1660, 1598 (quinone) cm^{-1}.

Anal. Calcd for $C_9H_8O_4$: C, 60.25; H, 4.47. Found: C, 60.35; H, 4.30.

2-(2′-Carbethoxyethyl)-1,4-benzoquinone was obtained as a bright yellow oil which crystallized on cooling with a Dry Ice–acetone mixture as long yellow needles, mp 11–15°; yield *ca.* 85%; ir 1730, 1253 (COOH), 1660, 1600 (quinone) cm^{-1}; nmr τ 3.25 (m), 5.82 (qu), 7.3 (m), and 8.74 ppm (t).[19]

1′,2′-Bis(2,5-dimethoxyphenyl)ethane (VI).—1,4-Dimethoxy-2-chloromethylbenzene [27.7 g (0.15 mol)] was dissolved in 120 ml of tetrahydrofuran. This solution was slowly added to a mixture of 1.82 g of magnesium turnings and 40 ml of tetrahydrofuran under vigorous stirring, the usual precautions for the preparation of Grignard compounds being taken. After the addition was finished, the reaction mixture was refluxed for 4 hr, tetrahydrofuran was distilled off, and the residue was heated to 100° for 2 hr on a steam bath. The reaction mixture was then acidified with 6 *N* hydrochloric acid and extracted with ether. Evaporation of the ether gave a slightly yellow oil which soon crystallized. Recrystallization from methanol gave white needles, mp 72°; yield 86%; nmr τ 3.29 (s), 6.20 (s), 6.28 (s), and 7.15 ppm (s).[19]

1′,2′-Bis(2,5-dihydroxyphenyl)ethane (I).—Compound VI, 8.0 g, was refluxed for 4 hr with 75 ml of 48% hydrobromic acid. From the filtered reaction mixture, dark brown crystals separated on cooling. Recrystallization from a large amount of boiling water gave white needles (4.0 g) which were further purified by sublimation at 200° (0.3 mm) bath temperature. They melted at 225° with decomposition. The same compound was simultaneously prepared by Manecke and Zerpner:[13] ir 3210, 1375, 1198 (OH), 1620, 1570, 1455 (aromatic ring) cm^{-1}.

1′,2′-Bis(2,5-benzoquinonyl)ethane (III).—Compound I, 1.2 g, in 50 ml of tetrahydrofuran was oxidized by stirring for 30 min with 5 g of silver oxide and 3 g of magnesium sulfate. The mixture was filtered rapidly, and the solvent was removed *in vacuo*. The dark brown residue, 1.0 g, was purified by sublimation at 160° (0.3 mm) bath temperature to yield microscopic yellow crystals, mp 194°; ir 1660, 1603 (quinone) cm^{-1}.

Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 69.18; H, 4.30.

Registry No.—2′-Hydroxyethyl-2,5-benzoquinone, 4082-30-8; III, 20452-50-0; IV, 20452-51-1; V, 10538-47-3; VI, 20306-76-7; 1,4-dihydroxy-2-(2′-carbethoxyethyl)benzene, 20452-54-4; 1,4-benzoquinone-2-(3′-propanoic acid), 20452-56-6; 2-(2′-carbethoxyethyl)-1,4-benzoquinone, 20452-57-7.

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Nuclear Magnetic Resonance Spectroscopy. Proton Spectra of Diallylmercury[1]

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Changes have been observed in the nmr spectra of diallylmercury as a function of temperature which seem explicable in terms of allylic rearrangement and intermolecular exchange. Analysis of the proton spectra of diallylmercury spectra using a modified LAOCOON II computer program gave coupling constant and chemical shift parameters which reproduced the spectra at 60, 100, and 220 MHz.

Analyses of the nmr spectra of three dipropenylmercury compounds have been reported with the objective of establishing their configurations and the stereochemistry of their preparation from propenyllithiums.[3] Similar studies of di-2-propenylmercury (diallylmercury) do not appear to have been published,[4] although it offers the additional possibility of undergoing both intermolecular and intramolecular exchange which, in principle at least, are distinguishable by nmr. Diallylmercury is expected to have a carbon–metal bond intermediate in ionic character between tetraallyltin[5] and diallylcadmium,[6] which have been found to exhibit $ABCD_2$ and AB_4 nmr spectra, respectively. The AB_4 spectra observed for allylmagnesium bromide and diallylmagnesium have been interpreted as indicating a rapid allylic rearrangement (either inter- or intramolecular) between the possible allylic isomers.[7]

It was of particular interest to investigate variations in the nmr spectra of diallylmercury with temperature to see whether rearrangement could be detected and whether or not such rearrangement occurs by intermolecular group exchange and can be distinguished from intramolecular rearrangement by disappearance or retention of the ^{199}Hg satellite lines in the progression

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[2] On sabbatical leave from Brooklyn College of the City University of New York, 1967–1968.

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