butyrolactone¹⁸ and γ, γ -dimethyl- γ -butyrolactone¹⁹ were prepared by published methods. The lactones were all freshly distilled at reduced pressure immediately before use, and their physical constants were in excellent agreement with published values. Their infrared spectra were determined in carbon tetrachloride solution using a Baird-Atomic double beam instrument.

Kinetics. Preliminary experiments showed that the saponification of γ -butyrolactone in 80% ethanol was too rapid (0.16 mole⁻¹ sec.⁻¹) to be conveniently followed by titration and to be rather too slow (0.0087 mole⁻¹ sec.⁻¹) in absolute ethanol. The measurements were accordingly carried out in 92.3% ethanol (d_{28}^{25} 0.8096), which had been purified by treatment with zinc dust and sodium hydroxide.

The lactone (0.2-0.3 g.) was dissolved in purified 92% ethanol (100-x ml.), allowed to equilibrate in a constant

(18) B. E. Hudson, Jr., and C. R. Hauser, J. Am. Chem. Soc., 63, 3156 (1941).

(19) R. T. Arnold, J. S. Buckley, Jr., and J. Richter, J. Am. Chem. Soc., 69, 2322 (1947); J. Cason, P. B. Brewer, and E. L. Pippen, J. Org. Chem., 13, 239 (1948); R. L. Frank, R. Armstrong, J. Kiviatek, and H. A. Price, J. Am. Chem. Soc., 70, 1379 (1948).

temperature bath at 25.08 \pm 0.02° or in an ice water bath at $0.00 \pm 0.02^{\circ}$ and 0.04M sodium hydroxide (x ml.) in the same solvent and at the same temperature added. Aliquots (10 ml.) were withdrawn at intervals, added to excess 0.06N hydrochloric acid (5 ml.) and ice-cold distilled water (20 ml.) and the excess acid immediately titrated with standard 0.045N sodium hydroxide solution, using phenolphthalein as indicator. The purity of the lactone was determined by dissolving samples (0.04-0.06 g.) in 0.045N aqueous sodium hydroxide (15 ml.) and titrating the excess base with standard acid after 2–3 days. The purity was always at least 95%and was taken into account in calculating the kinetics. The rate constants were determined from the slope of the second order rate plots in the usual manner. Each run was carried out at least three times and the means and their mean errors are given in Table I. The E act and log PZ values are probably accurate to ± 0.2 units.

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Electron Exchange Polymers. XV. NMR Spectra of Some Methylated Hydroquinones and Their Derivatives¹

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NMR spectra are reported on the *tau* scale for 1,4-dimethoxybenzene; 2-methyl-, 2,5-dimethyl-, 2,3,5-trimethyl-, and 2,3,5,6-terramethyl-1,4-dimethoxybenzenes; 2-vinyl-3,6-dimethyl- and 2-vinyl-3,5,6-trimethyl-1,4-dimethoxybenzenes; 2-(2-hydroxyethyl)-, 2-(2-hydroxyethyl)-3,6-dimethyl-, 2-(2-hydroxyethyl)-3,5-6-trimethyl-, and 2-(1-hydroxyethyl)-3,5,6-trimethyl-1,4-dimethoxybenzene; and $\alpha_{\alpha}\alpha'$ -bis(2,5-dimethoxy-3,4,6-trimethylphenyl)diethyl ether. The chemical shifts of the aromatic, methoxyl, and methyl protons are interpreted.

The use of NMR spectra has increased rapidly since the initial work of Purcell and co-workers,³ and its application to structural organic chemistry by Gutowsky and co-workers.⁴ Detailed discussions of theory and applications may be found in the works of Pople and co-authors,⁵ Roberts,⁶ Conroy,⁷ and Jackman.⁸ With this rapidly increasing use of NMR

(1) (a) Taken from the Dissertation submitted by Kenneth A. Kun to the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree. (b) For other papers in this series see K. A. Kun and H. G. Cassidy, J. Polymer Sci., 44, 383 (1960).

(2) Present address: Rohm and Haas Company, Research Laboratories, Bristol, Pa.

(3) E. M. Purcell, H. C. Torrey, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

(4) L. H. Meyer, A. Saika, and H. S. Gutowsky, J. Am. Chem. Soc., 75, 4567 (1953).

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance*, McGraw-Hill, New York (1959).

(6) J. D. Roberts, Nuclear Magnetic Resonance, McGraw-Hill, New York (1959).

(7) H. Conroy, "Nuclear Magnetic Resonance in Organic Structural Elucidation," in Advances in Organic Chemistry, Methods and Results, R. Raphael, ed., Interscience, New York (1960). it seemed of interest to report the chemical shifts of the aromatic methoxyl and methyl protons of several methylated hydroquinones and their derivatives.

Measurements described in this paper were made with a 60 mc./sec. Varian NMR spectrometer using analytical grade carbon tetrachloride as the solvent. All chemical shifts were measured with reference to an internal standard, tetramethylsilane, and are given on the "tau" (τ) scale as described by Tiers.⁹ The numbers of parentheses indicate relative intensities. Concentrations of 40% by volume were used. As a result, no bulk-susceptibility corrections are required, but some dilution effects characteristic of aromatic compounds are no doubt present.⁵

⁽⁸⁾ L. M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Pergamon Press, New York (1959).

^{(9) (}a) G. V. D. Tiers, J. Phys. Chem., 62, 1151 (1958);
(b) G. V. D. Tiers, Characteristic Nuclear Magnetic Resonance "Shielding Values" for Hydrogen in Organic Structures. Part I. Tables of τ-Values for a Variety of Organic Compounds. Exploratory NMR Studies. Project 737602, Central Research Department, Minnesota Mining & Manufacturing Co., St. Paul, Minn.

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Table I gives the chemical shifts of methylated hydroquinone dimethyl ethers; Table II gives the chemical shifts of vinyl methylhydroquinone dimethyl ethers, and Table III gives the chemical shifts of α - and β -hydroxyethylmethylhydroquinone dimethyl ethers.

TABLE I CHEMICAL SHIFTS OF METHYLATED HYDROQUINONE DIMETHYL ETHERS

Types of Protons			
Aromatic	Methoxyl	Methyl	
- <u></u>			
3.33 (2)	6.34 (3)		
3.44, 3.51 (1) (2)	6.34, 6.38 (3) (3)	7.8 (3)5	
3.53 (1)	6.30 (3)	7.88 (3)	
3.65 (1)	6.33, 6.48 (3) (3)	$\begin{array}{ccc} 7.81, \ 7.88, \\ (3) & (3) \\ 7.95 \\ (3) \end{array}$	
—	6.46 (3)	7.89 (6)	
	Aromatic 3.33 (2) 3.44, 3.51 (1) 3.53 (1) 3.65 (1)	Image: Aromatic Image: Method of the system 3.33 6.34 (2) (3) 3.44, 3.51 6.34, 6.38 (1) (2) 3.53 6.30 (1) (3) 3.65 6.33, 6.48 (1) (3) 3.65 6.33, 6.48 (1) (3)	

TABLE II CHEMICAL SHIFTS OF VINYL METHYLHYDROQUINONE DIMETHYL ETHERS

	Types of Protons			
	Aro- matic	Methoxyl	Methyl	
CH ₃ CH=CH ₂ CH ₃ CH=CH ₂ CH ₃ CH=CH ₂	3.43 (1)	6.34, 6.47 (3) (3)	7.81, 7.88 (3) (3)	
$\begin{array}{c} \text{OCH}_3\\ \text{CH}_3\\ \text{CH}_3\\ \text{CH}_3\\ \text{OCH}_3\\ \text{OCH}_3 \end{array}$		6.45, 6.50 (3) (3)	7.84, 7.90 (3) (6)	

The compounds studied were prepared as follows. 2,5-Dimethoxytoluene was prepared from *p*-toluhydroquinone by treatment in absolute methanol with dimethyl sulfate and methanolic potassium hydroxide. The preparation of 1,4-dimethoxy-2,5dimethylbenzene and 1,4-dimethoxy-2,3,5-trimethylbenzene will be described elsewhere.¹⁰ 1,4-(1,4-dimethoxy-2,3,5,6-tetra-Dimethoxydurene methylbenzene)¹¹ was prepared from 1,4-dimethoxy 2,6 - di(chloromethyl) - 3,6 - dimethylbenzene¹² by treatment with lithium aluminum hydride in ether. The preparations of the two methoxymethyl-substituted styrenes (Table II) and the methoxymethyl-substituted α - and β -hydroxyethylbenzenes (Table III) will be reported.¹⁰ β -Hydroxyethylhydroquinonedimethyl ether was prepared by the method of Barnes,13 according to which hydroquinone dimethyl ether was treated first with n-butyllithium and then with ethylene oxide.

From Table I several generalizations concerning the aromatic methyl and methoxyl protons may be suggested. Pople, Schneider, and Bernstein⁵ discussed aromatic protons on a variety of aromatic hydrocarbons and on substituted benzenes. They state, "The spectra of the ring protons of the methyl-substituted benzenes consist essentially of one unresolved signal, the only compound in which pronounced separation of signals is apparent being *m*-xylene. The position of the ring-hydrogen signal and methyl group signal in the field does vary, however, with substitution." Analogously with methyl-substituted 1,4-dimethoxybenzenes the aromatic protons consist of one unresolved peak with the exception of 2,5-dimethoxytoluene where there are two peaks, one of which is twice as large as the other. (A coupling constant of 1.5 cycles was observed for the *meta* proton). As with *m*-xylene the separation of signals is due to differences in environment of the ring-protons. Here also the position of ring-hydrogens varies with substitution. Increasing the number of methyl substituents in the ring increases the up-field shift of the aromatic protons. Similarly, for methyl substitution in hydroquinone dimethyl ethers, the methyl proton of the spectrum has a single peak with the exception of the unsymmetrical trimethylated compound (1,4-dimethoxy-2,3,5-trimethylbenzene). Here, as with the unsymmetrical ring protons, the methyl peak is resolved into more than one signal. In this case three peaks are found indicating the resolution of each methyl group, that is, the three methyl groups are different. This is easily shown by comparing the groups ortho, meta and para to each methyl group. Signals due to methoxyl protons suggest a variation due to the number of methyl groups ortho to the methoxyl group. 1,4-Dimethoxy-2,3,5-trimethylbenzene is shown to have two different methoxyl groups, one at 6.33 τ and the other at 6.48 $\tau.$ One of these methoxyl groups is ortho to a methyl group and an

(12) The preparation of this compound will be reported shortly.

(13) R. A. Barnes, J. Am. Chem. Soc., 75, 3004 (1953).

⁽¹⁰⁾ K. A. Kun and H. G. Cassidy, "Electron Exchange Polymers XVII," J. Polymer Sci., in press.

⁽¹¹⁾ L. I. Smith and H. C. Miller, [J. Am. Chem. Soc., 64, 440 (1942)] give the melting point of the compound.

	Types of Protons				
			Methyl		
	Aromatic	Methoxyl	Aromatic	Aliphatic	
OCH ₃ CH ₂ CH ₂ OH	3.20, 3.33 (1) (2)	6.33, 6.36 (3) (3)	_		
CH ₃ OCH ₃ OCH ₃ CH ₂ CH ₂ OH CH ₃ CH ₃	3.58 (1)	6.34, 6.37 (3) (3)	7.81, 7.86 (3) (3)		
$CH_3 \rightarrow CH_2CH_2OH$ $CH_3 \rightarrow CH_3 CH_3$ $CH_3 \rightarrow CH_3$		6.54, 6.58 (3) (3)	7.84, 7.91 (3) (6)		
$CH_{3} \rightarrow CHCH_{3}$ $CH_{3} \rightarrow CHCH_{3}$ $CH_{3} \rightarrow CHCH_{3}$ $CH_{3} \rightarrow CH_{3}$	_	5.97, 6.08 (3) (3)	7.77, 7.90 (3) (3)	8.59 (3)	

TABLE III CHEMICAL SHIFTS OF SOME α - and β -Hydroxyethylhydroquinone Dimethyl Ethers

aromatic hydrogen while the other is ortho to two methyl groups. One may differentiate between the two by comparing the chemical shifts of the methoxyl group with 1,4-dimethoxy-2,5-dimethylbenzene and 1,4 - dimethoxy - 2,3,5,6 - tetramethylbenzene. The former has methoxyl groups ortho to a methyl group and an aromatic proton, while the latter has methoxyl groups ortho to two methyl groups. As shown in Table I, the methoxyl group in 1,4-dimethoxy-2,5-dimethylbenzene is located at 6.30 τ and in 1,4-dimethoxy-2,3,5,6-tetramethylbenzene the absorption is observed at 6.46 τ . The difference in chemical shifts between the values 6.30 and 6.33 τ and 6.46 and 6.48 τ is probably due to an inductive and/or steric effect of the 3-methyl group in 1,4dimethoxy-2,3,5-trimethylbenzene. This effect, naturally, would be absent from 1,4-dimethoxy-2,5dimethylbenzene and may or may not be present in 1,4-dimethoxy-2,3,5,6-tetramethylbenzene. Coupling effects of a methyl group which does not have another methyl group para to it may be shown in the case of 2,5-dimethoxytoluene. The chemical shifts of these methoxyl protons were found at 6.34 and 6.38 τ while the chemical shift of the methoxyl protons of 1,4-dimethoxybenzene is 6.34τ . Therefore, it is strongly suggested that for 1,4-dimethoxy-2,3,5-trimethylbenzene the methoxyl group having a methyl group and an aromatic hydrogen in the ortho positions has a chemical shift at 6.33 τ and the methoxyl group with two methyl groups in ortho positions has a chemical shift at 6.48 τ . Analogous trends may be suggested for the substituted sty-

renes described in Table II and the substituted α and β -hydroxyethylbenzenes.

The spectra of the vinyl group in the substituted styrenes showed the twelve strong lines of the ABC (approximately ABX) system,¹⁴ —CH_x = CH_A H_B, which comprise three symmetrically split quartets.^{9a} For example, the vinyl group of 2,5dimethoxy-3,4,6-trimethylstyrene has a set of peaks whose quartets are centered at the following τ values: (X) 3.28, (A) 4.43, and (B) 4.67 with splittings: (X) 10.2 and 17.8 c.p.s.; (A) 1.2 and 17.4 c.p.s.; and (B) 1.2 and 10.2 c.p.s. Coupling between geminal protons A and B within the trigonally hybridized methylene group is expected to be small as in styrene,⁵ p-methylstyrene,¹⁵ and vinylanthraquinone.¹⁶

The α -hydroxyethyl group shows a characteristic pattern whereby the methine is split by the three methyl hydrogens to give a quadruplet and the methine proton splits the methyl group to give a doublet. For 2,5-dimethoxy-3,4,6-trimethyl- α -hydroxyethylbenzene, the aliphatic methyl signal is a doublet centered at 8.59 τ and the methine signal is a quadruplet centered at 6.48 τ .



⁽¹⁴⁾ H. J. Bernstein, J. A. Pople, and W. G. Schneider, Canadian J. Chem., 35, 65 (1957).

Using this information in conjunction with infrared and microanalytical data, α, α' -bis(2,5-dimethoxy-3,4,6-trimethylphenyl)diethyl ether¹⁰ was identified by its NMR spectrum. The methine proton is located at 5.05 τ and is split into a quadruplet by an alpha methyl group. This



methyl group is split by the methine proton to give a doublet which is found at 8.77 τ . The methoxyl and aromatic methyl groups are located at 6.41 and 6.75 τ and 7.76, 8.02, and 8.08 τ , respectively.

EXPERIMENTAL

The melting points and boiling points given in this study are uncorrected. All reagents used were of the highest purity available, either purified, reagent or analytical reagent grades.

Preparation of 2,5-dimethoxytoluene. Fifty grams of ptoluhydroquinone was dissolved in a solution of 250 ml. of absolute methanol and 504 g. of freshly distilled dimethyl sulfate. The solution was heated to reflux temperature and refluxing was continued for 15 min. Removing the heat source, refluxing was continued by adding methanolic potassium hydroxide (600 g. dissolved in 1.5 l. of methanol) so as to maintain a steady reflux rate. When the resulting reaction mixture was alkaline to litmus paper, the product was isolated by steam distilling it from the reaction mixture. Extraction of the distillate with ether, drying the organic fraction over anhydrous potassium carbonate, filtering and removing the solvent *in vacuo* from the filtrate yielded 53 g. of crude product. This material was distilled to give 50 g.

(15) R. W. Fessenden and J. S. Waugh, Abs. 132nd Meeting, American Chemical Society, Sept. 1957, p. 72 P.
(16) M. F. Refojo, Y. L. Pan, K. A. Kun, and H. G.

Cassidy, J. Org. Chem., 25, 416 (1960).

(82%) of a colorless liquid boiling at 46 to 51° at 0.2 mm, (lit. b.p.¹⁷ 214–218°).

Preparation of 1,4-dimethoxydurene. One gram of 1,4dimethoxy - 2,5 - dichloromethyl - 3,6 - dimethylbenzene¹² was refluxed for 4 hr. with an excess of lithium aluminum hydride in 25 ml. of absolute ether. The unchanged lithium aluminum hydride was decomposed with ethyl acetate and then the metal complex was destroyed with water. After removing the metal hydroxides by filtration, the filtrate was stripped of solvent *in vacuo* and the resulting residue was steam distilled. The desired product, 1,4-dimethoxydurene, was isolated by extracting the distillate with ether, drying the ether solution over anhydrous potassium carbonate, filtering, removing the solvent from the filtrate *in vacuo*, and crystallizing the residue from methanol. The product, a white crystalline solid, melted at 114-115°. (lit. m.p.¹¹ 112-115°).

Preparation of β -hydroxyethylhydroquinone dimethyl ether. Eight grams of 1,4-dimethoxybenzene was dissolved in 50 ml. of absolute ether and an excess of 0.994N n-butyllithium was added with stirring. The reaction mixture was stirred overnight. Four grams of ethylene oxide was added drop-wise to the reaction mixture, keeping the reaction temperature below 5°. The reaction mixture was slowly brought to room temperature and stirred for an additional 4 hr. The organometallic complex was decomposed with very dilute hydrochloric acid, the ether fraction separated and the aqueous fraction was extracted, with ether. Drying the combined ether fractions over anhydrous potassium carbonate, filtering, and distilling the solvent in vacuo from the filtrate yielded 7.8 g. of crude residue. This residue was distilled to yield 6.0 g. of product boiling at 115-6° at 0.2 mm. (b.p.¹⁸ 130-142° at 0.7 mm.).

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(17) I. Heilbron and A. M. Bunbury, *Dictionary of* Organic Compounds, Oxford University Press, New York, 1953.

(18) M. F. Refojo, unpublished work.

[CONTRIBUTION FROM THE EXPLOSIVES DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & CO.]

Reactions of Ferrocyanic and Cobalticyanic Acids

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Hexacyanoferric(II) and hexacyanocobaltic(III) acids yield when heated with an aliphatic alcohol an isonitrile complex which in the presence of excess of hydrogen cyanide gives the corresponding isonitrile. The esterification of hexacyanoferric (II) acid and the displacement of the alkyl isonitrile from the isonitrile complex may be combined into one reaction.

The acids of complex cyanides such as hexacyanoferric(II)¹ hexacyanoferric(III),² hexacyanocobal-

(1) F. Hölzl, Z. Elektrochem., 43, 319 (1937).

(2) J. Brigando, Bull. soc. chim. France, 503 (1957).

tic(III),² and hexacyanochromic(III)² acids are known to be strong acids approximating hydrochloric acid in strength. When heated with alcohols, hexacyanocobaltic(III)^{1,3} and hexacyanoferric-