Compound	$n^{22}D$	B.p. °C.	Mm.	Bromine, % Calcd.	Bromine, % Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl γ-bromobutyrate	1.4582	40	1	44.2	42.0	33.2	32.7	4.97	4.45
		78	10						
		105	40						
Methyl ε-bromohexanoate	1.4635	72	1	38.5	38.5	40.2	39.2	6.22	6.04
		100	5						
		112	10						

extracted with 95% ethanol. The ethanol-insoluble product was washed with water and dried. The dry product, 2.5 g., was polymeric. The ethanol-soluble material was separated by concentrating the solution and was recrystallized from absolute ethanol. The yield was 4.3 g., m.p. 68–69° (literature for ε-caprolactam, 69°).

Thermal Condensation of Methyl ε-Bromohexanoate.—Thirty ml. of methyl ε-bromohexanoate was heated at 200° under a nitrogen purge for 6 hr. During this time 7.0 ml. of methyl bromide was liberated (theoretical, 9.6 ml.). Only 0.001 mole of hydrogen bromide was evolved. The final product was a dark viscous oil. Upon distillation, 5 g. of a clear liquid (b.p. 62–129° (1 mm.)) was removed. The dark residue contained 17.0% bromine. The distillate which was clear and contained 24.0% bromine was largely the dimer, $Br(CH_2)_5CO_2(CH_2)_5CO_2CH_3$.

Preparation of Methyl ε-Cyanohexanoate from Methyl ε-Bromohexanoate and Alkali Cyanides.—Forty-one grams (0.2 mole) of methyl-ε-bromohexanoate, 15 g. (0.23 mole) of potassium cyanide and 300 ml. of anhydrous ethanol were refluxed while being stirred in a 3-necked flask for 16 hr. After the precipitated salts were filtered off, the solution was distilled to yield 12.54 g. of the nitrile ester (b.p. 119–125° (3 mm.)). Calcd. for $C_8H_{13}O_2N$: N, 9.04. Found: N, 9.04. Only 7.5 g. of unreacted bromoester was recovered.

When this reaction was repeated with only an 8-hr. reflux time, 8.6 g. of the nitrile ester was recovered and 17.3 g. of unreacted bromoester was recovered.

When sodium cyanide was used in place of potassium cyanide, after a 16-hr. reflux, 11.2 g. of nitrile ester and 17.9 g. of unreacted bromoester were obtained.

When potassium cyanide was used and the alcohol was replaced with dioxane as solvent, after a 16-hr. reflux no nitrile ester was obtained and 40 g. of unreacted bromoester was recovered.

Acknowledgments.—The authors wish to express appreciation to Mr. Oliver D. Smith, who carried out the bromine analyses, Mr. Wiley Crawford for the infrared analyses, Dr. Zoila Reyes for the synthesis of ε-caprolactam, Mr. Ernest Bishop for assistance in the telomerization runs, and to Drs. Bruce Graham, C. M. Himel and O. F. Senn of Stanford Research Institute and Drs. A. P. Giraitis and W. E. Foster of the Ethyl Corporation for valuable suggestions during the course of the work.

MENLO PARK, CALIF.

[CONTRIBUTION NO. 1401 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Electron Exchange Polymers. X. A General Method for the Preparation of Phenolic Polystyrenes[1a]

BY ROBERT STERN[1b] JAMES ENGLISH, JR., AND HAROLD G. CASSIDY

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A general method for the preparation of phenolic polystyrenes and the corresponding monomers is described. Vinylhydroquinone bis-methoxymethyl ether (V) was obtained in 60% yield from hydroquinone in a three-step synthesis; catechol gave similarly 3-vinylcatechol bis-methoxymethyl ether (VI), and *p,p'*-biphenol afforded *p,p'*-biphenol bis-methoxymethyl ether (X). The structure of these monomers was verified. All three monomers could be polymerized; the molecular weights of the macromolecules were determined osmometrically. Mild hydrolysis of the acetal groups afforded, for the first time, analytically pure polyvinylhydroquinone, 3-polyvinylcatechol and 3-polyvinyl-*p,p'*-biphenol.

Introduction.—Among the numerous investigations devoted to styrene derivatives,[2] vinylphenols and particularly dihydric vinylphenols are but rarely represented, probably because few, if any, of the pertinent synthetic methods[3] can be applied successfully to their formation. In the category of styrenes of dihydric phenols the formation of both 4-vinylcatechol[4] and 4-vinylresorcinol[5] has been claimed, but neither compound has been characterized and structurally authenticated. On the other hand, vinylhydroquinone (II) has been synthesized by two independent four-step processes,[6] the over-all yield in both methods being rather low. Because hydroxylated polystyrenes have attracted attention as electron exchangers[6,7] and novel polyelectrolytes, we wish to report a general method for the synthesis of these macromolecules and their monomers.

Synthetic Results.—Even though a carbanion would be unstable in the presence of as powerful an oxidizing agent as *p*-benzoquinone, it seemed

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(1)(a) Abstracted from Part I of the dissertation submitted by Robert Stern in February, 1956, to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Part of the material of this paper was first presented before the Division of Organic Chemistry, 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954, Abstracts of Papers, p. 102-O. (b) Department of Chemistry, Wesleyan University, Middletown, Conn.

(2) R. H. Boundy and R. F. Boyer, "Styrene," Reinhold Publishing Corp., New York, N. Y., 1953.

(3) W. S. Emerson, *Chem. Revs.*, **45**, 347 (1949).

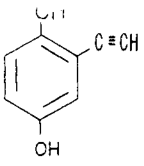
(4) H. Pauly and K. Neukam, *Ber.*, **41**, 4151 (1908).

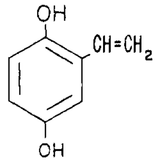
(5) V. L. Vaĭser, *Doklady Akad. Nauk S.S.S.R.*, **74**, 57 (1950); *C. A.*, **45**, 3828a (1951).

(6) (a) H. G. Cassidy, THIS JOURNAL, **71**, 402 (1949); (b) I. H. Updegraff and H. G. Cassidy, *ibid.*, **71**, 407 (1949); (c) D. D. Reynolds, J. A. Cathcart and J. L. R. Williams, *J. Org. Chem.*, **18**, 1709 (1953).

(7) (a) J. Schubert in "Annual Review of Physical Chemistry," Vol. V, Annual Reviews, Inc., Stanford, Calif., 1954, p. 416; (b) M. von Stackelberg in E. Müller's "Methoden der Organischen Chemie" (Houben-Weyl), Vol. III, Part 2, 4th ed., Georg Thieme Verlag, Stuttgart, 1955, p. 284; (c) H. C. Thomas and G. R. Frysinger in "Annual Review of Physical Chemistry," Vol. VII, Annual Reviews, Inc., Stanford, Calif., 1956, p. 151.

nonetheless attractive to attempt the 1,4-addition of sodium acetylide to this substance, for such a reaction, if successful, would afford 2,5-dihydroxyphenylacetylene (I), partial hydrogenation of which should yield vinylhydroquinone (II). This approach appeared promising because Grignard reagents and organolithium compounds have been reported to yield 1,2- *and* 1,4-addition products with various benzoquinones[8a,b] and naphthoquinones,[8a,c] despite the fact that reduction of these quinones by otherwise non-reducing Grignard reagents has also been recorded[8] in the past. Under our reaction conditions, however, *p*-benzoquinone yielded no 1,4-addition products with sodium acetylide[9]; reduction occurred, and the quinone and quinhydrone isolated from the reaction mixture accounted for 92.5% of the starting material.


I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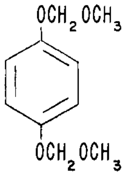
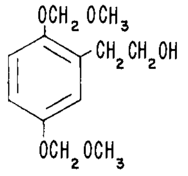
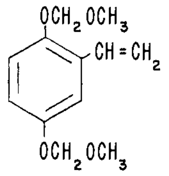
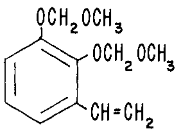

III

Because it was not possible to introduce the unsaturated side chain by this one-step reaction, a gradual building up of the vinyl group had to be envisaged. Unprotected phenolic functions react with organometallic reagents, and dihydric phenol derivatives are unstable in the presence of alkali, in addition to being powerful inhibitors in free radical polymerizations; it was, therefore imperative to block the hydroxyl functions of the phenols with a protecting group that would suffer cleavage under very mild conditions. The blocking groups could be neither esters nor ethers, for the former react with organometallic reagents while the latter do not cleave under mild conditions.[10] Tetrahydropyranyl ethers (mixed diacetals) did not prove to be useful blocking groups in this particular case,[11] and, consequently, we turned our attention to other acetals, in particular to the bis-methoxymethyl ethers of dihydric phenols.

Hydroquinone bis-methoxymethyl ether (III), reported but not characterized in an early German patent,[12] could be obtained in 93% yield by a two-stage acetalization of hydroquinone with chloromethyl methyl ether. When III was subjected to hydrogen–lithium exchange by means of *n*-butyllithium and subsequently treated with ethylene oxide, β-hydroxyethylhydroquinone bis-methoxymethyl ether (IV) was obtained in 85% yield. Dehydration of IV by means of potassium hydroxide afforded vinylhydroquinone bis-methoxymethyl ether (V) in 76% yield, the over-all yield of this three-step process amounting to 60%. Application of the same synthetic method to catechol yielded similarly 3-vinylcatechol bis-methoxymethyl ether (VI).


IV


V


VI

The identity of V follows clearly from the elementary analysis, acid solvolysis to vinylhydroquinone, hydrogenation and solvolysis to ethylhydroquinone and the infrared absorption spectrum. The latter exhibits peaks at 3010 (3.33 μ) and 908 cm.$^{-1}$ (11.0 μ) characteristic[13] in monosubstituted vinyl groups, *e.g.*, styrenes, of carbon–hydrogen stretching vibrations and of out-of-plane deformations of the hydrogens of the $=CH_2$ group. Similarly, the structure of VI follows from the elementary analysis, quantitative bromination in carbon tetrachloride solution, hydrogenation and solvolysis to 3-ethylcatechol, and the infrared absorption spectrum which exhibits the characteristic peaks of styrenes at 3010 (3.33 μ) and 909 cm.$^{-1}$ (10.99 μ). Furthermore, since without known exception an aromatic ether linkage is able to direct hydrogen–lithium exchange[14] *ortho* to itself if the ring system does not bear other substituents, it is inferred that the vinyl group occupies position three of the aromatic ring. The same conclusion also follows from the ultraviolet absorption spectrum of the ethylcatechol obtained from VI through hydrogenation and solvolysis. Indeed, it has been observed[15] that substitution of alkyl groups in position four of catechol results in *bathochromic spectral shifts* of about 5 mμ and that a similar effect is not obtained with the isomeric 3-substituted compounds. Thus 4-methylcatechol,[15] 4-*n*-amylcatechol[15] and 4-*t*-butylcatechol[16] absorb, respectively, at 282 (log ϵ 3.53), 282 (log ϵ 3.58) and 281 mμ (log ϵ 3.48), while catechol,[16] 3-*n*-propyl-

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[8] (a) For a comprehensive list of references *cf.* M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954, pp. 160–166, 529–548; (b) H. M. Crawford and M. McDonald, THIS JOURNAL, **71**, 2681 (1949); (c) H. M. Crawford, *ibid.*, **70**, 1081 (1948).

[9] This observation was confirmed quite recently by W. Ried and H. J. Schmidt, *Angew. Chem.*, **69**, 205 (1957). They reported that the reaction of quinones with acetylene, in the presence of sodium dissolved in liquid ammonia, proceeds in the direction of 1,2-addition; products such as I could apparently not be isolated from the reaction mixtures.

[10] Benzyl ethers, known to undergo hydrogenolysis under mild conditions (W. H. Hartung and R. Simonoff, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 263–326), were not considered suitable for our synthetic purpose because of the highly probable interference of the benzylic hydrogen atoms and/or the benzylic aromatic ring in metalation reactions. Thus, benzyl methyl ether rearranges to phenylmethylcarbinol upon treatment with phenyllithium, while benzyl phenyl ether undergoes fission and transformation into 1,1,2-triphenylethane when subjected to similar reaction conditions. *Cf.* (a) A. Lüttringhaus and G. von Sääf, *Angew. Chem.*, **51**, 918 (1938); (b) G. Wittig and L. Löhmann, *Ann.* **550**, 260 (1942); (c) G. Wittig and W. Happe, *ibid.*, **557**, 206 (1947); (d) G. Wittig, H. Döser and I. Lorenz, *ibid.*, **562**, 192 (1949).

[11] R. Stern, J. English, Jr., and H. G. Cassidy, THIS JOURNAL, **79**, 5797 (1957).

[12] P. Hoering and F. Baum, German Patent 209,608. In P. Friedlaender's "Fortschritte der Teerfarbenfabrikation," Vol. IX, Verlag Julius Springer, Berlin, 1911, p. 904.

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 31.

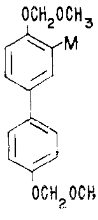
[14] H. Gilman and J. W. Morton, Jr., "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 258.

[15] R. Adams, C. K. Cain and H. Wolff, THIS JOURNAL, **62**, 732 (1940).

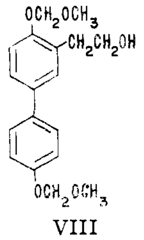
[16] H. S. Mason, *ibid.*, **70**, 138 (1948).

catechol[16] and 3-*n*-pentadecylcatechol[16] display principal absorption at 277 (log ϵ 3.36), 276 (log ϵ 3.35) and 277 mμ (log ϵ 3.32). The ethylcatechol obtained in this study has maximum absorption at 277 mμ (log ϵ 3.37) in ethanol; this constitutes strong evidence that it *is* 3-ethylcatechol and that the corresponding monomer is a 3-vinylcatechol derivative.

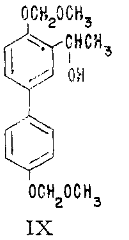
p,p'-Biphenol has one of the highest oxidation–reduction potentials, 954 mvolts, recorded for organic compounds,[17] and hence it was of great interest to prepare electron exchange macromolecules of this type. The bis-methoxymethyl ether of *p,p'*-biphenol (VIIa) could not be obtained in higher yields than 72% and was accompanied always by small amounts of *p,p'*-biphenol monomethoxymethyl ether, *p,p'*-$CH_3OCH_2O–C_6H_4–C_6H_4–OH$. Reaction of the lithium compound VIIb of the bis-methoxymethyl ether with ethylene oxide gave only a 2.5% yield of β-hydroxyethyl-*p,p'*-biphenol bis-methoxymethyl ether (VIII). Furthermore, it is characteristic that the reaction of VIIb with freshly purified acetaldehyde afforded α-hydroxyethyl-*p,p'*-biphenol bis-methoxymethyl ether (IX) in similarly low yields of only 11%. These results could not be altered by using an excess of ethylene oxide or acetaldehyde or by carrying out the reaction in 1,2-dimethoxyethane. Since this singular unreactivity of the organometallic compound VIIb was due to its insolubility in the reaction medium,[11] the bis-methoxymethyl ether VIIa was metalated (incompletely) for only five minutes and the resulting supersaturated solution of VIIb was subjected immediately, before precipitation of VIIb would begin, to the action of ethylene oxide; in this manner the pure reaction product VIII could be obtained in 28% yield. Dehydration of VIII afforded 3-vinyl-*p,p'*-biphenol bis-methoxymethyl ether (X). The infrared spectrum exhibits the characteristic absorption of monosubstituted vinyl groups, as discussed earlier, at 908 cm.$^{-1}$ (11.0 μ). Here again, as a consequence of the hydrogen–lithium exchange and by analogy with other organolithium metalations, the vinyl group is assigned an *ortho* position to the hetero-atom.



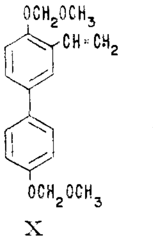
VIIa, M = H
b, M = Li



VIII



IX



X

Polymerization and Solvolysis.—All three monomeric bis-methoxymethyl ethers V, VI and X underwent polymerization in the presence of benzoyl peroxide catalyst. The number-average molecular weights of the corresponding polymers, determined by osmometric measurements, were 88,300 ± 1200, 429,000 ± 29,000 and 51,400 ± 800; they differed widely in the three cases due to variation of the polymerization conditions.

The protecting groups of the macromolecules were solvolyzed quantitatively in cold 10% methanolic hydrochloric acid; evaporation of the solvent at *room temperature* afforded polyvinylhydroquinone, 3-polyvinylcatechol and 3-polyvinyl-*p,p'*-biphenol. The molecular weights, as calculated from those of the unsolvolyzed polymers, were 53,600 ± 700, 260,000 ± 17,600 and 31,300 ± 600, respectively. These unprotected polymers were insoluble in organic solvents, could be redissolved only with difficulty in methanolic hydrochloric acid and were extremely hygroscopic,[18] so that good analytical values could be obtained only when moisture was excluded with meticulous care. Polyvinylhydroquinone, the only polymer of this type reported in earlier investigations, has never been obtained before as an analytically pure sample. That all three phenolic polymers could be isolated in this investigation as analytically pure materials was due chiefly to the relatively mild and quantitative hydrolysis of the acetal protecting groups. This then constitutes one of the main virtues of the synthetic method presented in this paper.

Our results indicate that it was possible by the synthesis described here to obtain for the first time a variety of hydroxylated polystyrenes. The method should certainly be applicable to compounds with unreactive halogen substituents (*e.g.*, chlorine) which do not undergo halogen–metal exchange with *n*-butyllithium. In compounds with reactive halogens, *e.g.*, bromine or iodine, the relative position of the halogen will determine whether metalation will proceed normally or *halogen*–metal exchange will take precedence[19] over *hydrogen*–metal interconversion.

Acknowledgments.—The authors wish to thank Professor Raymond M. Fuoss for very helpful discussions and for most of the equipment used in the osmometric determination of molecular weights. The financial assistance of the Research Corporation is gratefully acknowledged.

Experimental[20]

Hydroquinone Bis-methoxymethyl Ether (III).—Sixty-six grams (0.6 mole) of pure hydroquinone dissolved in 200 ml. of anhydrous methyl alcohol was added to a cooled solution of 13.8 g. (0.6 gram atom) of metallic sodium in 200 ml. of absolute methanol under strict exclusion of moisture and oxygen. The monosodium salt of hydroquinone was soluble in methanol. The temperature of the orange solution was maintained at 0° while 48.3 g. (0.6 mole) of chloromethyl methyl ether was added dropwise under a steady stream of nitrogen. A 3.0-g. excess of chloromethyl methyl ether was necessary to achieve a *p*H of 8, and great care was taken not to acidify the reaction mixture beyond this point.

The successive addition of 13.8 g. (0.6 gram atom) of sodium and of 48.3 g. (0.6 mole) of chloromethyl methyl ether was repeated three more times in the manner described above. The resulting mixture was stirred overnight, the precipitated sodium chloride was filtered and the solvent was evaporated on the steam-bath. The residue, dissolved in 300 ml. of ether, was extracted three times with 10% aqueous sodium hydroxide. The ether layer afforded 110.0 g. (92.5%) of crude ($n^{25.0}$D 1.4956) III. Fractional distillation through a one-foot jacketed column packed

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[17] L. F. Fieser, THIS JOURNAL, **52**, 4915 (1930).

[18] This would seem to indicate that strong hydrogen bonding occurs between phenolic groups which are not attached to the same aromatic ring.

[19] H. Gilman, W. Langham and F. W. Moore, THIS JOURNAL, **62**, 2327 (1940).

[20] All melting points are corrected. The boiling points are uncorrected.

with helices gave 105.0 g. of a colorless liquid, b.p. 75° (0.3 mm.), $n^{25.0}D$ 1.4972. *Anal.* Calcd. for $C_{10}H_{14}O_4$: C, 60.60; H, 7.11. Found: C, 60.52; H, 7.05.

The compound was further identified by solvolysis to hydroquinone: One gram of III dissolved in 30 ml. of pure methanol was refluxed for 3 hr. with 1.0 g. of Amberlite IR-112 cation exchange resin.[21] The solvent was evaporated after filtering the resin; the crystalline residue, 0.52 g. (95%), yielded on recrystallization from methanol and benzene 0.48 g. of white needles, m.p. 170°. A mixed melting point with authentic hydroquinone showed no depression.

When hydroquinone bis-methoxymethyl ether was prepared without using a 100% excess of chloromethyl methyl ether, the yield dropped from 92.5 to 26.7%. It was also attempted to prepare III by first forming the disodium salt of hydroquinone in methanol (in which it is insoluble), replacing the methanol by benzene through azeotropic distillation and then adding the equivalent amount of chloromethyl methyl ether. Hydroquinone bis-methoxymethyl ether was obtained by this method in only 16.1% yield.

Catechol Bis-methoxymethyl Ether.—The experimental conditions and the quantities of reagents used in the preparation of this compound were exactly the same as those described for III. The crude product, 105.0 g. (88% yield), afforded on distillation 92.0 g. of pure catechol bis-methoxymethyl ether, b.p. 85° (0.4 mm.), $n^{25.0}D$ 1.5019. *Anal.* Calcd. for $C_{10}H_{14}O_4$: C, 60.60; H, 7.11. Found: C, 60.45; H, 6.96.

The compound was further identified by solvolysis to catechol, m.p. 105°, using the method described in the identification of hydroquinone bis-methoxymethyl ether. A mixed melting point with authentic catechol showed no depression.

***p,p'*-Biphenol bis-methoxymethyl ether (VIIa)** was prepared by the same method as the corresponding hydroquinone di-acetal, except that a threefold excess of sodium and of chloromethyl methyl ether was used up in six successive additions. Sixty-one grams (0.33 mole) of *p,p'*-biphenol gave 65.0 g. (72.5%) of crude crystalline product which on distillation yielded 57.0 g. of VIIa, b.p. 175–185° (1.2 mm.), m.p. 58–64°. Pure, colorless VIIa melted at 69.2–70.4° after six crystallizations from high boiling petroleum ether. *Anal.* Calcd. for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.09; H, 6.52.

***p,p'*-Biphenol Mono-methoxymethyl Ether.**—This compound was isolated from the alkaline extracts obtained in the preparation of *p,p'*-biphenol bis-methoxymethyl ether. These aqueous washings were acidified by large amounts of solid carbon dioxide, and the resulting solution was extracted with ether. The ether phase gave 4.9 g. of crude *p,p'*-biphenol mono-methoxymethyl ether, m.p. 135–136°. Three crystallizations from benzene raised the melting point to 138.0–139.0°. *Anal.* Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 73.20; H, 6.35.

β-Hydroxyethylhydroquinone Bis-methoxymethyl Ether (IV).—Lithium–hydrogen exchange was carried out under standard conditions[14] between 59.5 g. (0.3 mole) of III, dissolved in 50 ml. of absolute ether and 360 ml. (0.32 mole) of 0.88 *N* *n*-butyllithium solution. After stirring the mixture for 24 hr., the reaction flask was fitted with a condenser cooled by solid carbon dioxide and 18.0 g. (0.41 mole) of ethylene oxide, placed into a small flask, was permitted to vaporize into the reaction vessel. The reaction mixture was stirred for 15 hr. and the ethereal solution was hydrolyzed. The organic layer afforded 76.0 g. of a liquid which was separated by vacuum distillation into essentially two fractions. The first fraction, 16.4 g., $n^{22.0}D$ 1.4978, b.p. 90–110° (0.6 mm.), constituted unchanged starting material, as evidenced by the infrared spectrum, while the second fraction, 45.7 g., $n^{22.0}D$ 1.5130 to 1.5152, b.p. 134–143° (0.6 mm.), proved to be crude IV and gave a positive alcohol test by the alkali-xanthogenate method.[22] Taking into account the recovered material, the yield amounted to 85.8% of theory. In another preparation the yield was 91.5%. Fractionation through a two-foot jacketed column packed with helices yielded pure IV, b.p. 173° (2.0 mm.), $n^{20.6}D$ 1.5149. *Anal.* Calcd. for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.45; H, 7.23.

The infrared absorption spectrum exhibits a broad absorption band at 3412 cm.$^{-1}$ (2.93 μ) due to associated oxygen–hydrogen stretching and a well noticeable shoulder at 1029 cm.$^{-1}$ (9.71 μ) due to oxygen–hydrogen deformation.

The 1-naphthylurethan was prepared[23] in the customary manner and was crystallized four times from *n*-hexane; m.p. 97.8–98.7°. *Anal.* Calcd. for $C_{23}H_{25}O_6N$: C, 67.13; H, 6.12; N, 3.42. Found: C, 67.23; H, 6.21; N, 3.64.

β-Hydroxyethylhydroquinone bis-methoxymethyl ether was further identified by acid hydrolysis to β-hydroxyethylhydroquinone.[11]

3-(β-Hydroxyethyl)-catechol Bis-methoxymethyl Ether.—This compound was prepared under experimental conditions identical to those used in the preparation of IV. Starting with 49.55 g. (0.25 mole) of catechol bis-methoxymethyl ether, there was obtained 59.0 g. of crude product which afforded 16.4 g. ($n^{25.0}D$ 1.5032, b.p. 80–125 at 0.4 mm.) of unchanged starting material, as evidenced by the infrared spectrum, and 29.2 g. of crude 3-(β-hydroxyethyl)-catechol bis-methoxymethyl ether, $n^{25.0}D$ 1.5130 to 1.5156, b.p. 130–140 (0.4 mm.), giving a positive test for alcohols by the alkali-xanthogenate method.[22] Taking into account the recovered material, the yield amounted to 72%. Fractionation through a one-foot jacketed Podbielniak type column afforded the pure compound, b.p. 124–127° (0.5 mm.), $n^{25.0}D$ 1.5144. *Anal.* Calcd. for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.68; H, 7.70.

The infrared spectrum exhibits a broad absorption band in the 3330–3570 cm.$^{-1}$ (2.8–3.0 μ) region due to oxygen-hydrogen stretching.

The 1-naphthylurethan was crystallized five times from *n*-heptane; m.p. 82.2–83.2°. Invariably the material would re-solidify a few degrees above this temperature and melt again at 94.5–95.5°. *Anal.* Calcd. for $C_{23}H_{25}O_6N$: C, 67.13; H, 6.12; N, 3.42. Found: C, 67.59; H, 5.86; N, 3.53.

3-(β-Hydroxyethyl)-*p,p'*-biphenol Bis-methoxymethyl Ether (VIII).—This compound was first prepared under the usual experimental conditions, as described for the similar compound in the hydroquinone series. From 2.75 g. (0.01 mole) of VIIa there was obtained 2.06 g. of an oily solid; the infrared spectrum was identical to that of the starting material. Fractional sublimation of this pasty solid afforded 0.08 g. of a colorless liquid coming over at 140° (0.2 mm.), which appeared to be slightly impure VIII according to the analysis and the infrared spectrum. The low yield of only 2.5% could not be improved by substituting anhydrous 1,2-dimethoxyethane for ether as solvent. The following modified procedure afforded VIII, however, in much better yields and in pure form:

Lithium–hydrogen exchange was allowed to proceed *for five minutes* between 22.0 g. (0.08 mole) of VIIa and 50 ml. (0.096 mole) of 1.91 *N* *n*-butyllithium solution. The metalation was carried out under standard conditions,[14] with the exception that the reaction flask had been fitted with a condenser cooled by solid carbon dioxide. When the *n*-butyllithium was added the solution assumed immediately an orange color and became somewhat opaque, but no precipitate appeared within the specified five minutes; 7 g. (0.16 mole) of ethylene oxide, dissolved in 20 ml. of absolute ether, was now added and the instantaneous exothermic reaction brought the solvent to boiling. After 40 minutes stirring the mixture was hydrolyzed; the organic phase afforded 24.0 g. of an oil mixed with crystals. Distillation from a Claisen flask yielded: (a) 8.3 g. of unchanged starting material, b.p. 168–175° (0.001 mm.), having an undepressed mixed melting point with authentic VIIa and an infrared spectrum identical in all respects to that of the latter; (b) a small intermediary fraction of 3.3 g., b.p. 175–213° (0.001 mm.); and finally (c) 10.3 g. of the crude product, b.p. 218–240° (0.001 mm.), in form of a yellow oil. Slow distillation of this last fraction from a small Claisen flask fitted with a fraction cutter afforded 4.5 g. (28% yield, counting the recovered starting material) of pure product, b.p. 213–214° (0.001 mm.), $n^{25.0}D$ 1.5753. It crystallized after many fruitless attempts from petroleum ether in beautiful colorless bushy needles, m.p. 67.0–68.0°, and exhibited depression of the melting point on mixing with starting material. *Anal.* Calcd. for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 68.14; H, 7.00.

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(21) Rohm and Haas Co., Philadelphia, Penna.

(22) F. Feigl, "Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 2nd ed., Akademische Verlagsgesellschaft, Leipzig, 1935, p. 366.

(23) N. D. Cheronis, "Micro- and Semimicro Methods," Vol. VI of A. Weissberger's "Technique of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 485–489, 497–499.

The infrared spectrum exhibits a broad absorption band at 3575 cm.$^{-1}$ (2.8 μ) due to associated oxygen–hydrogen stretching. The 1-naphthylurethan, m.p. 109–110°, was crystallized twice from *n*-heptane. *Anal.* Calcd. for $C_{29}H_{29}O_6N$: C, 71.44; H, 6.00. Found: C, 71.06; H, 6.26.

3-(α-Hydroxyethyl)-*p,p'*-biphenol Bis-methoxymethyl Ether (IX).—The preparation of this compound was carried out under experimental conditions identical to those used in the synthesis of III with the only exception that freshly distilled acetaldehyde (0.8 g. or 0.02 mole) was used as one of the reagents instead of ethylene oxide. Starting with 2.75 g. (0.01 mole) of VIIa there was obtained 2.5 g. of crude product. Fractional sublimation of this pasty solid afforded: (a) 1.26 g. of unchanged starting material, as evidenced by the infrared spectrum, coming over at 70–92° (0.2 mm.), m.p. 63–69°; (b) 0.27 g. of an intermediary fraction; and (c) 0.36 g. (11% yield) of an oil coming over at 128–132° (0.2 mm.) and representing slightly impure reaction product IX. *Anal.* Calcd. for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.39; H, 6.95.

The infrared spectrum exhibits a broad absorption band at 3575 cm.$^{-1}$ (2.8 μ) due to associated oxygen–hydrogen stretching. The α-naphthylurethan, crystallized three times from *n*-heptane, melted at 110–111°. *Anal.* Calcd. for $C_{29}H_{29}O_6N$: C, 71.44; H, 6.00; N, 2.87. Found: C, 71.28; H, 5.76; N, 3.09.

Vinylhydroquinone Bis-methoxymethyl Ether (V).—The general dehydration procedure of Sabetay as modified by Marvel and Hein was followed.[24] In a 300-ml. two-necked flask, fitted with a dropping funnel and a small still-head with receiver, was placed 70 g. of U.S.P. potassium hydroxide pellets; a few boiling stones were added and a very small amount of picric acid was introduced to act as a polymerization inhibitor. The apparatus was pumped out to about 5 mm. pressure and the reaction flask heated at 230° in a Wood's metal bath. When the evolution of vapors had subsided and the potassium hydroxide in the flask had almost completely solidified, 36.36 g. (0.15 mole) of IV was added dropwise over a period of about 45 minutes. The crude distillate, 33.0 g., afforded, after redistillation in the presence of a small amount of picric acid, 25.4 g. (75.5%) of pure V, b.p. 106.5–107.5° (0.1 mm.), $n^{23.0}D$ 1.5257. *Anal.* Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.04; H, 7.25.

The material obtained in another run boiled at 113–114° (0.25 mm.), $n^{23.0}D$ 1.5263.

Vinylhydroquinone (II) from Vinylhydroquinone Bis-methoxymethyl Ether.—A solution of 3.36 g. (0.15 mole) of V in 20 ml. of pure methanol containing one small drop of concd. hydrochloric acid was refluxed for 1 hr. on the steam-bath under a stream of nitrogen. The chilled solution was neutralized carefully (*p*H 6) by means of 2% alcoholic potassium hydroxide solution. The alcohol was evaporated in vacuum, the residue was taken up in boiling benzene and the solution was filtered from insoluble matter, largely polymeric in nature. On cooling, the solution afforded a mixture of oil and crystals, 1.2 g., which solidified almost completely at 0°. A few pure crystals, 0.10 g., could be scraped off; on crystallization they melted at 110°. The infrared spectrum of this material was identical in every respect with that of authentic[6b] vinylhydroquinone. A mixed melting point, 109–110°, with authentic II showed no depression.

The rest of the impure crystal mixture was subjected to vacuum sublimation at 80°; 100 mg. of the oily solid yielded 60 mg. of white crystals, m.p. 106–107°. After one crystallization from benzene the solid melted at 109–110°, and the mixed melting point with authentic vinylhydroquinone showed no depression.

Ethylhydroquinone from Vinylhydroquinone Bis-methoxymethyl Ether.—A solution of 1.35 g. (6.0 millimoles) of V in 50 ml. of pure methanol was treated with hydrogen at atmospheric pressure in the presence of 305 mg. of Adams catalyst. The compound absorbed 142.0 ml. of hydrogen under standard conditions; the calculated amount is 148.0 ml. The hydrogenation mixture was decanted from the catalyst and the solvent evaporated. The residue, a somewhat viscous colorless liquid, was redissolved in 60 ml. of pure methanol and refluxed for 2 hr. with 1.0 g. of Amberlite IR-112 cation exchange resin.[21] The cation exchanger was filtered, and the solvent was evaporated; the residue, 0.70 g. (84% yield), afforded colorless prisms, m.p. 113°, on crystallization from benzene. Authentic ethylhydroquinone[25] melts at 113–114°.

3-Vinylcatechol Bis-methoxymethyl Ether (VI).—The dehydration of 3-(β-hydroxyethyl)-catechol bis-methoxymethyl ether (7.27 g., 0.03 mole) was carried out under the same conditions as the one described above for the corresponding hydroquinone derivative. The crude product, 4.3 g. (63%), afforded 3.5 g. of pure, colorless VI, b.p. 101–105° (0.65 mm.), $n^{24.0}D$ 1.5257. *Anal.* Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.36; H, 7.34.

3-Vinylcatechol bis-methoxymethyl ether (0.448 g., 2.0 millimoles) dissolved in carbon tetrachloride absorbed 2.2 millimoles of bromine. The oily dibromo compound (0.770 g., 100%) obtained after evaporation of the solvent was not characterized.

3-Ethylcatechol from 3-Vinylcatechol Bis-methoxymethyl Ether.—The hydrogenation of VI was carried out under the same conditions as the corresponding reduction of V. In the presence of 214 mg. of Adams catalyst 0.673 g. (3.0 millimoles) of VI absorbed 77.0 ml. of hydrogen under standard conditions; the calculated amount is 74.0 ml. After hydrolysis of the acetal groups by means of Amberlite IR-112 cation exchange resin,[21] 0.34 g. (81%) of oily 3-ethylcatechol, λ_{max} 277 mμ (log ϵ 3.37) in ethanol, was obtained. It was characterized in form of its bis-*p*-nitrobenzoate prepared[26] from 0.15 g. (1.1 millimoles) of 3-ethylcatechol and 0.44 g. (2.4 millimoles) of freshly crystallized *p*-nitrobenzoyl chloride in 1.5 ml. of dry pyridine. The crude derivative was crystallized three times from acetone as slightly yellow needles, m.p. 139.6–140.4°. *Anal.* Calcd. for $C_{22}H_{16}O_8N_2$: C, 60.55; H, 3.70; N, 6.42. Found: C, 60.77; H, 3.92; N, 6.18.

3-Vinyl-*p,p'*-biphenol Bis-methoxymethyl Ether (X).—The dehydration of 3.2 g. (0.01 mole) of VIII was carried out under the experimental conditions described earlier in a 15-ml. flask to which an addition funnel and a distillate receiver had been sealed. The crude product, 2.6 g., afforded on distillation 1.8 g. (60%) of pure X, b.p. 190° (0.001 mm.), $n^{25.0}D$ 1.5882. *Anal.* Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.69; H, 6.89.

Polyvinylhydroquinone Bis-methoxymethyl Ether.—Into a small glass tube, flushed with pure nitrogen, was placed 0.45 g. (2.0 millimoles) of V dissolved in 1.75 g. of distilled dry toluene. To this 20% monomer solution was added 0.0048 g. (0.02 millimole or 1.0 mole per cent.) of pure benzoyl peroxide; the tube was sealed and heated for 60 hr. at 85°. The tube was then opened and the polymer was precipitated by addition of pure methanol. Half the solvent was evaporated in a stream of nitrogen at room temperature, the polymer was redissolved in benzene and the precipitation procedure was repeated two more times. This removed the unreacted monomer, as well as low molecular weight polymers, by virtue of their solubility in methanol. Lyophilization from benzene solution resulted in 0.31 g. (69%) of a white and fluffy material. *Anal.* Calcd. for $(C_{12}H_{16}O_4)_n$: C, 64.27; H, 7.19. Found: C, 64.04; H, 7.33.

3-Polyvinylcatechol Bis-methoxymethyl Ether.—The polymerization of VI was carried out with 0.90 g. (4.0 millimoles) of monomer dissolved in 1.35 g. of distilled dry toluene (40% solution), in the presence of 0.0024 g. (0.01 millimole or 0.25 mole per cent.) of benzoyl peroxide catalyst. The mixture was heated for six days at 48–52°. The polymer was isolated in the same way as the corresponding hydroquinone derivative. A perfectly white and fluffy material, 0.51 g. (56.7%), was obtained. *Anal.* Calcd. for $(C_{12}H_{16}O_4)_n$: C, 64.27; H, 7.19. Found: C, 64.57; H, 7.10.

3-Polyvinyl-*p,p'*-biphenol Bis-methoxymethyl Ether.—The polymerization of X was carried out with 0.90 g. (3.0 millimoles) of monomer dissolved in 1.35 g. of dry toluene (40% solution), in the presence of 0.0036 g. (0.015 millimole or 0.5 mole per cent.) of benzoyl peroxide catalyst. The mixture was heated for 60 hr. to 60°. The method of isolation of the polymer was the same as that used in the polymerization of the corresponding hydroquinone derivative. The white and fluffy material weighed 0.31 g. (34% yield).

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(24) (a) S. Sabetay, *Bull. soc. chim. France*, [4] **45**, 69 (1929); (b) C. S. Marvel and D. W. Hein, THIS JOURNAL, **70**, 1895 (1948); (c) W. S. Emerson, *Chem. Revs.*, **45**, 353 (1949).

(25) T. B. Johnson and W. W. Hodge, THIS JOURNAL, **35**, 1014 (1913).

(26) See p. 494 of Ref. 23.

TABLE I

OSMOMETRIC DETERMINATION OF MOLECULAR WEIGHTS

	$^a\lim_{c\to 0} \pi/c$	$\bar{M}_n$	$\bar{X}$
Bis-methoxymethyl ether of			
Polyvinylhydroquinone	0.277 ± 0.004	88,300 ± 1,200	390 ± 6
3-Polyvinylcatechol	.057 ± .004	429,000 ± 29,000	1910 ± 130
3-Polyvinyl-*p,p'*-biphenol	.477 ± .007	51,400 ± 800	171 ± 3
Polystyrene IV(3(2-1-49))	.310 ± .021	79,200 ± 5,200	762 ± 50

[a] In atm. cm.^{3} g.$^{-1}$.

Anal. Calcd. for $(C_{18}H_{20}O_4)_n$: C, 71.98; H, 6.71. Found: C, 72.00; H, 6.28.

Polyvinylhydroquinone.—In about 30 ml. of 10% methanolic hydrochloric acid, obtained by bubbling anhydrous gaseous hydrochloric acid through redistilled C.P. methanol, was dissolved 22.4 mg. (0.1 millimole) of polyvinylhydroquinone bis-methoxymethyl ether. Hydrogen was slowly bubbled through this solution *at room temperature* for five days. The solvent was then evaporated in a stream of hydrogen and the residue dried for 24 hr. in an Abderhalden apparatus in vacuum (0.1 mm.) over boiling toluene. The vacuum was cut with nitrogen and the flask containing the sample, 13.6 mg. (100% of theory), sealed into a tube filled with pure nitrogen. Because the compound is extremely hygroscopic, good analytical values could only be obtained when the sample was dried again just before analysis and weighed in a special balance under nitrogen atmosphere. *Anal.* Calcd. for $(C_8H_8O_2)_n$: C, 70.57; H, 5.92. Found: C, 70.42; H, 6.06.

3-Polyvinylcatechol.—3-Polyvinylcatechol bis-methoxymethyl ether, 33.6 mg. (0.15 millimole), was hydrolyzed under identical conditions as the corresponding hydroquinone polymer. *Very careful drying* afforded 20.4 mg. (100%) of 3-polyvinylcatechol. *Anal.* Calcd. for $(C_8H_8O_2)_n$: C, 70.57; H, 5.92. Found: C, 70.07; H, 5.76.

3-Polyvinyl-*p,p'*-biphenol.—3-Polyvinyl-*p,p'*-biphenol bis-methoxymethyl ether, 30.0 mg. (0.1 millimole), was hydrolyzed under identical conditions as the corresponding hydroquinone polymer. On *very careful drying* 21.2 mg. (100%) of the hydrolyzed polymer was obtained. *Anal.* Calcd. for $(C_{14}H_{12}O_2)_n$: C, 79.22; H, 5.70. Found: C, 78.90; H, 5.47.

Osmometric Determination of Molecular Weights.—The osmotic pressure data were determined at 25.00° by the static elevation method,[27] using an instrument designed by Zimm and Myerson.[28] Calculation of the data was based[27] on the equation $\pi/c = RT(1/\bar{M}_n + Bc + \dots)$, neglecting higher than linear terms; π symbolizes the osmotic pressure, c the concentration, R the gas constant, T the absolute temperature, $\bar{M}_n$ the number-average molecular weight of the solute and B the second virial coefficient of the expansion of π/c as a function of c.

The osmometer was calibrated with a standard sample IV (3(2-1-49)) of polystyrene of the International Union of Pure and Applied Chemistry (courtesy of Professor Raymond M. Fuoss), the number-average molecular weight of which had been determined[29] to be 79,000. In the present calibration a value of 79,200 ± 5200 was obtained. The perfect agreement of these two results is fortuitous, because the validity of the measurements is limited by the estimated error of 5200 or 6.5%.

The osmometric measurements made on polyvinylhydroquinone bis-methoxymethyl ether, 3-polyvinylcatechol bis-methoxymethyl ether and 3-polyvinyl-*p,p'*-biphenol bis-methoxymethyl ether (in toluene solution) are summarized in Table I. The intercept $RT/\bar{M}_n = \lim_{c\to 0} \pi/c$ of all three π/c *vs.* c plots was determined algebraically by the method of least squares. The corresponding number-average molecular weights, $\bar{M}_n$, and number-average degrees of polymerization, $\bar{X}_n$, are also listed in Table I.

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(27) R. H. Wagner, in A. Weissberger's "Physical Methods of Organic Chemistry," Vol. I, Part I, 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1949, pp. 488–491, 512–514, 517–519 and 532.

(28) B. H. Zimm and I. Myerson, THIS JOURNAL, **68**, 911 (1946).

(29) H. P. Frank and H. Mark, *J. Polym. Sci.*, **10**, 139 (1953).

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[CONTRIBUTION NO. 1369 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Diastereomeric Tetrahydropyranyl Ethers of Hydroquinone[1a]

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The reaction of hydroquinone with 2,3-dihydropyran is shown to lead to a mixture of *two* diastereomeric bis-2-tetrahydropyranyl ethers, a result not observed by previous workers. The two isomers have been separated, identified and their configurations tentatively assigned on the basis of melting point comparisons. Both form lithium compounds which react with carbon dioxide but not with ethylene oxide; this unreactivity is shown to be due to insolubility of the lithium derivatives.

Introduction.—In the formation of 2-tetrahydropyranyl ethers[2,3] an hydroxyl function is added across the double bond of 2,3-dihydropyran, a process which effects the formation of a new asymmetric center; hence, molecules containing an asymmetric carbon atom (*e.g.*, sterols) and molecules permitting the introduction of more than one tetrahydropyran ring (*e.g.*, dihydric phenols) should yield a mixture of diastereoisomeric (diameric) tetrahydropyranyl ethers. Only one case has been reported in which two isomeric steroidal 2-tetrahydropyranyl ethers have actually been isolated and reasonably well characterized,[4] yet the available experimental evidence and physical data[5] suggest that usually sterols afford *varying* mixtures of two diastereomeric

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(1) (a) Abstracted from Part II of the dissertation submitted by Robert Stern in February, 1956, to the Graduate School of Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) Department of Chemistry, Wesleyan University, Middletown, Conn.

(2) G. F. Woods and D. N. Kramer, THIS JOURNAL, **69**, 2246 (1947).

(3) W. E. Parham and E. L. Anderson, *ibid.*, **70**, 4187 (1948).

(4) E. Elisberg, H. Vanderhaeghe and T. F. Gallagher, *ibid.*, **74**, 2814 (1952).

(5) See, for instance: (a) W. G. Dauben and H. L. Bradlow, *ibid.*, **74**, 559 (1952); (b) A. C. Ott, M. F. Murray and R. L. Pederson, *ibid.*, **74**, 1239 (1952); (c) C. W. Greenhalgh, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 1190 (1951).