[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Pentenyl-, Hexenyl- and Heptenylresorcinols

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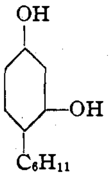
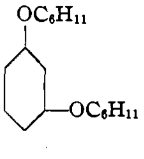
Hexylresorcinol has been studied considerably in recent years but no attention has been given to its unsaturated analogs. The allylresorcinols[2] are the only alkenylresorcinols to have been investigated although the hexenyl- and heptenylpyrogallols have been described recently.[3]

In the synthesis of 4-hexenylresorcinol (A), 1-bromo-2-hexene was reacted with resorcinol and potassium carbonate in acetone solution.


(A)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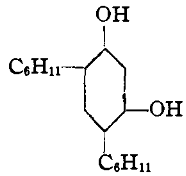
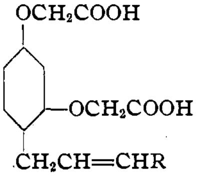
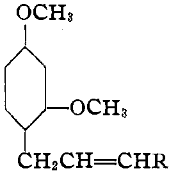

(C)

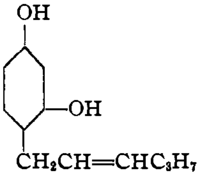
Concurrently, there was formed resorcinol hexenyl diether (B), which was separated by insolubility in alkali, and 4,6-dihexenylresorcinol (C) which was separated from (A) by its lower volatility. The pentenyl- and heptenylresorcinols were prepared analogously. A molecular still was advantageous for the distillation of these substances. The alkenylresorcinols were characterized by solid derivatives (D) with chloroacetic acid. The methyl diethers (E) were also synthesized.

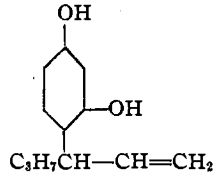

(D)

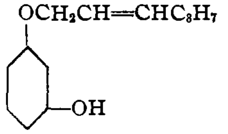

(E)

The structure of the alkenyl group in these compounds is a matter of some interest. Obviously, it is related to the structure of the alkenyl bromide used in the synthesis. Instead of regarding this as pure 1-bromo-2-alkene as has been done in the past,[4] it should be regarded as an equilibrium mixture of 1-bromo-2-alkene and 3-bromo-1-alkene, the former predominating. This aligns the structure with that of "crotyl" bromide, which has been proved[5] to be an equilibrium mixture of 1-bromo-2-butene and 3-bromo-1-butene, with the former in considerable excess.

On this basis, (A) should be regarded as a mixture of F + G. It is reasonably certain that (A) was formed from resorcinol by direct substitution. Therefore, the F:G ratio should approximate the ratio of the two substances in hexenyl bromide. Hydrogenation of the (F + G) mixture yielded a mixture of hexylresorcinols from which *n*-hexylresorcinol crystallized.


(F)


(G)


(H)

Structure (G) might be regarded as coming from the ether (H) by pyrolysis. On heating, (H) should rearrange into (G) but temperatures of 200–220° would be required whereas 100° was the maximum temperature in this work. Both (B) and (H)[6] have been shown to be stable at 100°.

The position of the hexenyl group in hexenylresorcinol was established by oxidizing the methyl diether (E) to 2,4-dimethylbenzoic acid.

Bactericidal data on the resorcinol derivatives were obtained through the courtesy of the Parke, Davis and Company Laboratories. The phenol coefficients toward three test organisms are listed in Table I. The values of two related compounds are included for comparison.

Experimental Part

Reagents.—The syntheses of 1-bromo-2-hexene and 1-bromo-1-heptene have been described.[6] That for 1-bromo-2-pentene was as follows. 1-Pentene-3-ol, b. p. 35–37° (20 mm.), was prepared in 78% yield by dropping a solution of acrolein in ether into an excess of ethylmagnesium bromide at −5°. Then a mixture of 121 g. of this alcohol, 350 g. of 48% hydrobromic acid and 100 g. of concd. sulfuric acid was stirred for twenty-four hours.

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(1) Parke, Davis and Company Fellow, 1931–1933.

(2) Hurd, Greengard and Pilgrim, THIS JOURNAL, **52**, 1700 (1930).

(3) Hurd and Parrish, *ibid.*, **57**, 1731 (1935).

(4) Bouis, *Ann. chim.*, [10] **9**, 421 (1928).

(5) Winstein and Young, THIS JOURNAL, **58**, 104 (1936).

(6) Hurd and Schmerling, *ibid.*, **59**, 107 (1937).

TABLE I

PHENOL COEFFICIENTS

Compound	Test organism *Staph. aureus* at 37.5°	 *Strep. hemol.* at 37.5°	 *B. typhosus* at 20.5°
Phenol	1	1	1
4-*n*-Hexylresorcinol[a]	98	. . .	56
Resorcinol *n*-hexyl monoether[a]	125	. . .	46
4-Hexenylresorcinol	150	200	40
4,6-Dihexenylresorcinol	>200	>200	>30
Mixture of 4-hexyl-resorcinol and isomers	150	125	. .
4-Pentenylresorcinol	20	. . .	. .

[a] Klarmann, Gatyas and Shternov, THIS JOURNAL, **53**, 3402 (1931). The temperature was 37°.

After dilution with water, the pentenyl bromide layer was separated, washed, dried and distilled. It boiled at 38–41° (19 mm.); $n^{21}\mathrm{D}$ 1.4757. The yield was 169 g. or 80%. It was chiefly 1-bromo-2-pentene but was probably in equilibrium with 3-bromo-1-pentene.

The Alkenylresorcinols

4-Hexenylresorcinol.—Forty-nine grams (0.3 mole) of 1-bromo-2-hexene was added during three hours to a well-stirred mixture of 66 g. of resorcinol (0.6 mole), 300 cc. of acetone and 40 g. of anhydrous potassium carbonate. The mixture was then refluxed for three hours. The acetone was removed by distillation and the residue was extracted with carbon tetrachloride. The resulting solution was washed free of resorcinol by many extractions with water. The alkali-soluble material was then separated from the mixture by use of a dilute solution of sodium hydroxide.

The alkaline solution was acidified with hydrochloric acid and the solution was extracted with ether. The extract was washed with water, dried and distilled from a Hickman molecular still[8] (p. 1732) at 0.003–0.005 mm. The bottom of the still was heated by a steam-bath. Thirty grams of distillate accumulated. It was redistilled. The first 23 cc. to come over (collected in several fractions) possessed a uniform index of refraction, $n^{25}\mathrm{D}$ 1.5388. That for the next 7 cc. was 1.5416. The 23-cc. portion, $d^{25}{}_4$ 1.0481, was hexenylresorcinol.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 75.0; H, 8.32. Found: C, 74.5; H, 8.32.

4-Pentenylresorcinol.—This was prepared similarly from 66 g. of resorcinol, 45 g. of 1-bromo-2-pentene, 40 g. of potassium carbonate and 300 cc. of acetone. Several arbitrary fractions were collected in the Hickman still and the index of refraction taken. Those of similar constants were combined and refractionated thrice. In this way, 7 g. of pentenylresorcinol, $n^{25}\mathrm{D}$ 1.5461, $d^{25}{}_4$ 1.0671, was obtained.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.92. Found: C, 73.9; H, 7.99.

4-Heptenylresorcinol.—The general details were similar, these quantities of reagents being used: 85.5 g. of 1-bromo-2-heptene (0.5 mole), 110 g. of resorcinol (1 mole), 60 g. of potassium carbonate and one liter of acetone. The preliminary fractionation was by vacuum distillation at 1 mm. There was 17 cc. at 138–143°, 11 cc. at 143–150°, 7 cc. at 150–170° and 3.5 cc. of residue. The 17-cc. fraction contained the bulk of the heptenylresorcinol, and the 7-cc. fraction contained some diheptenylresorcinol (see below). Subsequent fractionations were performed in the Hickman still (at 100°) and 14 cc. of product, $n^{25}\mathrm{D}$ 1.5360, was obtained.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 75.7; H, 8.80. Found: C, 75.5; H, 8.79.

The Diethers

Resorcinol Hexenyl Diether, $C_6H_4(OC_6H_{11})_2$.—The carbon tetrachloride solution from which 4-hexenylresorcinol had been extracted was distilled in a Hickman still at 100° after it was washed free of alkali and dried. Seven grams of a mobile liquid was obtained, $n^{25}\mathrm{D}$ 1.5172, $d^{25}{}_4$ 0.9634.

Anal. Calcd. for $C_{18}H_{26}O_2$: C, 78.8; H, 9.48. Found: C, 78.4; H, 9.50.

Resorcinol Pentenyl Diether.—This diether was obtained similarly from the carbon tetrachloride solution from which 4-pentenylresorcinol had been extracted. The distillate from the Hickman still weighed 3.5 g.; $n^{25}\mathrm{D}$ 1.5227, $d^{25}{}_4$ 0.973.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.0; H, 9.01. Found: C, 78.3; H, 9.01.

Chloroacetic Derivatives of the 4-Alkenylresorcinols

2,4-Di-(carboxymethoxy)-1-hexenylbenzene (Structure D).—One gram of 4-hexenylresorcinol, 3.5 g. of chloroacetic acid and an excess of 10% sodium hydroxide solution were heated on a steam-bath for an hour. The solution was cooled, acidified and extracted with ether. The extract was washed with water and extracted with a solution of sodium bicarbonate. On acidification of the bicarbonate extract, the desired acid precipitated. After several crystallizations from 50% methanol it melted at 159–160°; yield 0.5 g.

Anal. Calcd. neut. equiv. for $C_6H_{11}C_6H_3(OCH_2COOH)_2$, 154. Found: 157.

2,4 - Di - (carboxymethoxy) - 1 - pentenylbenzene.—The m. p. of this derivative, prepared similarly from 4-pentenylresorcinol, was 164–165°.

Anal. Calcd. neut. equiv. for $C_5H_9C_6H_3(OCH_2COOH)_2$, 147. Found: 150.

2,4 - Di - (carboxymethoxy) - 1 - heptenylbenzene.—This acid, similarly prepared, melted at 144–145°.

Anal. Calcd. neut. equiv. for $C_7H_{13}C_6H_3(OCH_2COOH)_2$, 161. Found: 162.

Hydrogenation of the Hexenylresorcinol.—Four grams of 4-hexenylresorcinol was hydrogenated catalytically using 0.15 g. of the Adams platinum oxide catalyst, 200 cc. of ethyl alcohol, and hydrogen. The hydrogenation took an hour, but most of the hydrogen was absorbed in the first fifteen minutes. After filtration, the material was distilled at 3 mm. Two cc. of distillate (b. p. 130–135°, $n^{25}\mathrm{D}$ 1.5320, $d^{25}{}_4$ 1.056) remained as an oil, but 0.6 cc. (b. p. 135–140°) solidified on standing. The latter melted at 67–68° which is the m. p. of 4-hexylresorcinol.[7] The 2-cc. fraction also analyzed correctly for hexylresorcinol but the fact that it would not crystallize, even

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(7) Dohme, Cox and Miller, THIS JOURNAL, **48**, 1688 (1926).

when seeded, indicated that the material was a mixture of *n*-hexylresorcinol and isomers, presumably 4-(α-ethylbutyl)-resorcinol and resorcinol *n*-hexyl monoether (formed via the hexenyl monoether). The phenol coefficient of this fraction was determined (Table I).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.2; H, 9.28. Found: C, 74.1; H, 9.33.

Methylation of the Alkenylresorcinols

4-Hexenylresorcinol Methyl Diether, $C_6H_{11}C_6H_3(OCH_3)_2$.—A mixture of 4.5 g. of 4-hexenylresorcinol, 50 cc. of 10% sodium hydroxide solution and 20 g. of methyl sulfate was stirred vigorously for an hour. The insoluble layer was drawn off, the aqueous layer was extracted with ether and the combined insoluble layers were washed with water, dried and distilled in a Hickman still at 100° and 0.12–0.15 mm.; yield 4.5 g. When redistilled at 10 mm. the material boiled at 150–152°; $n^{7}\text{D}$ 1.5233, $n^{25}\text{D}$ 1.5154, $d^{25}{}_4$ 0.9865.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.4; H, 9.09. Found: C, 76.3; H, 9.02.

4-Pentenylresorcinol Methyl Diether.—4-Pentenyl-resorcinol (2.7 g.) was dissolved in 35 cc. of 10% sodium hydroxide solution and an excess of methyl sulfate was added. The mixture was stirred for one hour. The methylated compound was separated and distilled in a Hickman still. At 0.0005 mm. and 100° the material distilled at the rate of 20–25 drops per minute. The yield was 2.5 g.; $n^{25}\text{D}$ 1.5192, $d^{25}{}_4$ 0.986.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.79. Found: C, 75.6; H, 8.72.

Oxidation to 2,4-Dimethoxybenzoic Acid.—Twenty grams of powdered potassium permanganate was added to a solution of 4.0 g. of 4-hexenylresorcinol methyl diether in 200 cc. of acetone (distilled from potassium permanganate). The mixture was heated on the water-bath and stirred mechanically. At the end of one hour the manganese dioxide was removed by filtration, 100 cc. of water was added and the acetone was removed by distillation. The solution became cloudy due to the precipitation of unoxidized material. This (0.35 g.) was removed by ether extraction. The water solution was made slightly acid with sulfuric acid and 1.3 g. of 2,4-dimethoxybenzoic acid[8] precipitated; m. p. after one crystallization, 108°.

4,6-Dihexenylresorcinol (Structure C).—Resorcinol (55 g., 0.5 mole) was added to a solution of sodium (6.9 g., 0.3 mole) in 400 cc. of absolute alcohol. Then, during two hours, 49 g. (0.3 mole) of 1-bromo-2-hexene was dropped into the stirred mixture. It was stirred for ten hours more and then refluxed for two hours. The solvent was distilled off, the residue extracted with carbon tetrachloride (100 cc.) and the extract washed repeatedly with water until free of resorcinol. It was dried and distilled at 3 mm. Forty grams was collected at 135–155°; residue, 4 g. It was redistilled at 3 mm. through a 15-cm. column, whereupon 25 g. of monohexenyl derivatives were removed in the first fractions. Then, 7.5 g. of dihexenylresorcinol was collected at 155–180°. The latter was redistilled in a Hickman still. The fraction thus obtained was analyzed; $n^{25}\text{D}$ 1.5310, $d^{25}{}_4$ 0.9971.

Anal. Calcd. for $C_{18}H_{26}O_2$: C, 78.82; H, 9.48. Found: C, 79.07; H, 9.46.

This compound was also prepared in work with Mr. Louis Schmerling as follows. A suspension was made of sodium resorcinolate (from 5.5 g. of resorcinol and 2.3 g. of sodium) in benzene (25 g.). Eight grams of 1-bromo-2-hexene in 35 cc. of benzene was added and the mixture stirred for ten hours. Then another 8 g. was added and the mixture refluxed for nine hours. The benzene solution was decanted from the sodium bromide and washed repeatedly with water. After evaporation of the benzene under diminished pressure the residue was treated with 175 cc. of Claisen's aqueous–alcoholic potash (a mixture of 53 g. of potassium hydroxide and 44 cc. of water, made up to 175 cc. with methanol). A 2-g. fraction of resorcinol hexenyl diether was separated.

The alkaline solution was acidified with dilute sulfuric acid. The resulting oil was ether extracted, washed, dried and distilled in a Hickman still at 100°. About 2 g. of hexenylresorcinol was collected first, then 3.5 g. of dihexenylresorcinol (mol. wt., 265; calcd. for $C_{18}H_{26}O_2$, 274).

4,6-Dihexenylresorcinol Methyl Diether, $(C_6H_{11})_2C_6H_2(OCH_3)_2$.—The dihexenylresorcinol (3.5 g.) was dissolved in 10% sodium hydroxide solution after which it was stirred for an hour with an excess of methyl sulfate. The oil which separated was taken up in ether, washed, dried and distilled. Three grams of the diether was obtained; b. p. 158–163° at 10 mm., $n^{25}\text{D}$ 1.5145, $d^{25}{}_4$ 0.957.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.4; H, 9.93. Found: C, 78.8; H, 10.0.

4,6-Diheptenylresorcinol, $(C_7H_{13})_2C_6H_2(OH)_2$.—This was a high-boiling by-product in the preparation of 4-heptenylresorcinol (see above). Its low volatility was witnessed by its slow rate of distillation from the Hickman still, namely, about one drop per minute at 100° and 0.0005 mm. Thus, from the less-volatile fractions there was finally obtained 2.5 cc. of oil which appeared to be 4,6-diheptenylresorcinol, $n^{25}\text{D}$ 1.5265.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.4; H, 9.93. Found: C, 79.1; H, 10.1.

Summary

This paper describes the preparation of hexenylresorcinol, pentenylresorcinol and heptenylresorcinol by direct substitution of resorcinol with the corresponding alkenyl bromide. Concurrent reaction products were the dialkenylresorcinols and the resorcinol alkenyl diethers. The use of a molecular still greatly facilitated the separation and purification of these compounds. Chloroacetic acid derivatives and methyl ethers of the alkenylresorcinols were prepared.

From the hexenylresorcinol some *n*-hexylresorcinol was prepared by hydrogenation. Oxidation of hexenylresorcinol methyl diether gave rise to 2,4-dimethoxybenzoic acid.

Bactericidal data are included.

EVANSTON, ILL. RECEIVED SEPTEMBER 21, 1936

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(8) Mauthner, *J. prakt. Chem.*, **210**, 43 (1921).