the sugar group have been made by Haworth, can be decided by experiment alone and the necessary data do not now exist.

27. Summary

It is shown that the measurements of Brauns on the aceto-halogeno derivatives of cellobiose and 4-glucosidomannose, taken in conjunction with the proof by Wolfrom and Lewis that normal tetramethylglucose and normal tetramethylmannose are true epimers, disprove Haworth's assumption that rings never shift during the methylation of glycosides. In consequence the whole system of ring structures which Haworth has built up for the simple and compound sugars, which is based upon this assumption, loses its foundation and the questions must be restudied through the use of evidence which avoids this invalid assumption. Such evidence is presented and the ring structures of many of the monosaccharides are disclosed through the application of the rules of optical superposition and isorotation.

Washington, D. C.

[Contribution from the Chemical Laboratory of Northwestern University]

THE BEHAVIOR OF ALLYL DERIVATIVES OF CATECHOL AND RESORCINOL TOWARD HEAT

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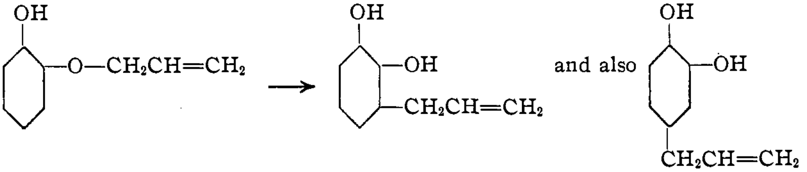
Received January 10, 1930 Published April 7, 1930

Except in a few instances, study of the pyrolytic rearrangement of allyl aryl ethers[1] has been confined to derivatives of monohydric phenols. In many such cases it has been observed that the allyl group wanders to an ortho carbon of the aromatic nucleus, thereby forming an *o*-allyl-phenol, unless both ortho positions are previously substituted, in which case the rearrangement proceeds normally to the para position.

Similar experiments with dihydric phenols have been little studied. In fact, when these experiments were undertaken in 1926 no work whatsoever had been published in this field. Two articles[2] have since appeared dealing with the mono- and diallyl ethers of catechol. The former has been shown to rearrange into both 3-allylcatechol and 4-allylcatechol, the former predominating.



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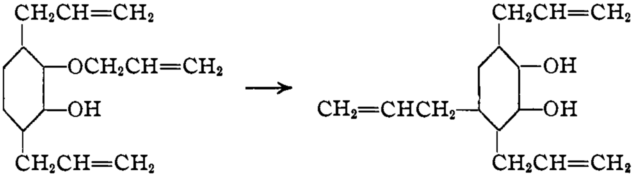
[1] For a survey of this topic, see Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., New York, **1929**, pp. 214–228.

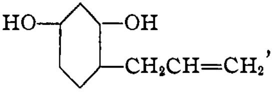
[2] Kawai, *Sci. Papers Inst. Phys. Chem. Res.*, **3**, 263 (1926); Perkin, Jr., and Trikojus, *J. Chem. Soc.*, 1663 (1927).

From the diallyl ether, Kawai obtained evidence for rearrangement into 3,5-diallylcatechol. Our work has included a similar study of these ethers and in addition several other allylcatechols have been synthesized and studied. Triallylcatechol was obtained in two ways: first, from the rearrangement of the monoallyl ether of diallylcatechol



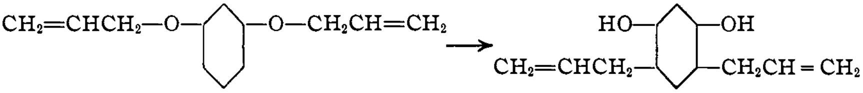
and, second, from the diallyl ether of monoallylcatechol. Tetra-allylcatechol was prepared by heating the diallyl ether of diallylcatechol.

Allyl Ethers of Resorcinol.—The monoallyl ether of resorcinol offers the interesting possibility of "ortho" rearrangement into either 1-allyl-2,4-dihydroxybenzene or 2-allyl-1,3-dihydroxybenzene, but only the former,



, appears to be formed. This was confirmed by methylation and oxidation into 2,4-dimethoxybenzoic acid. Several attempts were made to oxidize the allyl-dimethoxy-benzene directly but all met with failure.[3] This oxidation was readily accomplished, however, by converting the allylresorcinol first into either propenylresorcinol or its dimethyl ether, $(CH_3O)_2C_6H_3CH{=}CHCH_3$, by heating with alkali. The last compound oxidized readily to 2,4-dimethoxybenzoic acid, the melting point of which was found to agree with the recorded value[4] of 108°. The alternative isomer, 2,6-dimethoxybenzoic acid, was clearly excluded by its high m. p.,[5] 179°.

Similarly, the diallyl ether of resorcinol[6] was found to undergo rearrangement at 210° into 1,5-diallyl-2,4-dihydroxybenzene



The diallyl ether of the latter compound still has two available nuclear carbon atoms, but one of them is meta. Therefore, it would be anticipated that but one of the allyl groups should be affected by the heating.

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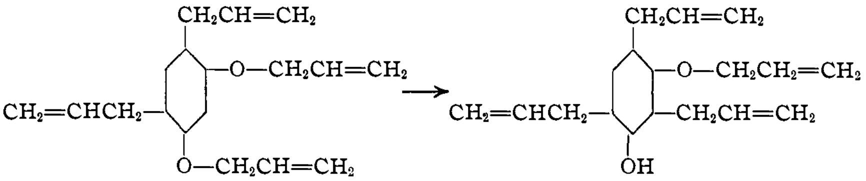
[3] Some of these trials were carried out by Mr. D. H. McQueen.

[4] Tiemann and Parrisius, *Ber.*, **13**, 2378 (1880); von Pechmann and Duisberg, *ibid.*, **16**, 2126 (1883).

[5] De Bruyn, *Rec. trav. chim.*, **2**, 222 (1883).

[6] Wilson and Adams, THIS JOURNAL, **45**, 533 (1923), prepared the diallyl ether of resorcinol, *m*-$C_6H_4(OCH_2CH{=}CH_2)_2$, from resorcinol-*bis*-(γ-bromopropyl) ether, *m*-$C_6H_4(OCH_2CH_2CH_2Br)_2$, by heating the latter to 225°. Some rearrangement of the diallyl ether into a diallylresorcinol may have occurred during this synthesis because of the high temperature, but this possibility seems not to have been studied.



It was definitely established that such was the case by proving that the resulting compound possessed but one hydroxy group and not two, by means of the phenyl isocyanate derivative.

Experimental Part

Monoallyl Ether of Resorcinol.—Only the preparation of this ether will be described in detail, but the general method of preparation for the others will be outlined.

Molar quantities of potassium carbonate and resorcinol were mixed in 200 cc. of acetone, with some evolution of heat. The flask containing this mixture was then fitted with a stirrer and attached to a reflux condenser. A mole of allyl bromide was added slowly and with constant stirring. When about three-fourths of it had been added, external cooling of the flask was necessary to prevent too vigorous boiling. The remaining allyl bromide was added with less evolution of heat. Refluxing on a water-bath with continual stirring was continued for four hours. After cooling, the solid material was filtered off and washed with 50 cc. of acetone. The washings were added to the first filtrate and the acetone was removed by distillation. A test portion of the residual oil was placed in a few cc. of sodium hydroxide solution. Since it seemed to dissolve completely, this demonstrated the absence of any great amount of the diallyl ether. The oil was then fractionally distilled, and the portion coming over up to 122° at 2 mm. was collected; yield, 112. 5 g. On redistillation, the main portion came over at 106–110° and 3 mm. A small portion (5 g.) of the diallyl ether was collected above 135°.

Analysis of the 106–110° (3 mm.) liquid for hydroxyl group with methylmagnesium iodide by the Zerewitinoff method revealed the presence of considerable resorcinol. In fact, resorcinol crystallized out of this distillate (and of other similar distillates) after a few days' standing. This admixed resorcinol was removed by shaking the mass with water. A little hydrochloric acid was found to be useful in breaking the emulsion thus produced. After drying over sodium sulfate, the pure monoallyl ether of resorcinol was then distilled. These physical constants were obtained: b. p. 122° at 2 mm.; 133° at 6 mm.; 141° at 33 mm.; n_D^{15} 1.5525; n_D^{30} 1.5474. Analysis of this material for hydroxyl indicated at least 99% purity. The yield of this purified material, based on the original resorcinol taken, was 27–30%.

Anal. (Zerewitinoff). Subs., 0.1820: CH_4 evolved, 0.0200 g. Calcd. wt. of CH_4 to be evolved from $HO\text{-}C_6H_4\text{-}OC_3H_5$, 0.0194.

Although the monoallyl ether of resorcinol distils as a colorless oil, it darkens considerably if it is kept bottled for two or three weeks.

General Method of Preparation of the Allyl Ethers.—In general, the catechol or resorcinol was refluxed[7] for four to five hours in acetone solution with the calculated quantity of allyl bromide and with a slight excess of fused potassium carbonate. For

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[7] This period of refluxing was necessary for good yields even where there was a considerable heat of reaction at the outset. With resorcinol, for example, a 46% yield of the diallyl ether was attained in fifteen minutes, as compared to an 83% yield in five hours.

convenience in working up the products, a minimum volume of acetone was usually taken. Ordinarily the weight of the catechol or resorcinol compound exceeded the weight of the solvent used. At the termination of the reflux period the mixture was diluted with three or four times its weight of water, the layer of oil which separated was removed, and the aqueous layer thrice ether-extracted. In the case of the diallyl ethers the combined extracts were twice washed with dilute alkali solution (5% sodium hydroxide) and then with water. After drying over anhydrous sodium sulfate or potassium carbonate, the ether was removed and the residual material fractionated *in vacuo*. For the monoallyl ethers this procedure was performed in the manner outlined above for the monoallyl ether of resorcinol. Purification by vacuum distillation was frequently impossible, because of prior rearrangement. In such cases the rearranged product was purified instead. The monoallyl ethers gave the characteristic color reactions with ferric chloride solution. They yielded no precipitate with lead acetate solution in acetone. The diallyl ethers formed no salts and gave no coloration with ferric chloride. A summary of results is given in Table I.

TABLE I

PREPARATION OF VARIOUS ALLYL ETHERS

Original subs. taken	Weight g.	Allyl ether formed	Yield		B. p., °C. (mm.)
			g.	%	
Catechol	22	Mono	17	70	108–113 (18)
Catechol	11	Di[a]	14–18	70–93	130–135 (18); 125–128 (10)
3-Allylcatechol	6	Mono	Rearranged during purification		
3-Allylcatechol	6	Di	Rearranged during purification		
3,6-Diallylcatechol	12	Di	8	47	180–185 (22) some dec.
Resorcinol	110	Mono[b]	38	27	122 (2); 133 (6); 141 (33)
Resorcinol	11	Di	14–16	75–83	149–153 (4); 160–165 (24)
4,6-Diallylresorcinol	11	Di	Rearranged during purification		

[a] Colorless, but turned yellow on standing. The ether possessed a penetrating, irritating odor. [b] Colorless, but darkened (brown) in two weeks. Similar irritating odor.

Pyrolysis of the Allyl Ethers of Catechol, Resorcinol and their Analogs. Properties of the Allylcatechols and of the Allylresorcinols.—In general it was only necessary to heat the allyl ethers to 175–210° (bath temperature) for rearrangement to occur. The reaction completed itself in a short time and in many cases was decidedly exothermic. The red color of the rearranged mass was characteristic. Furthermore, the original sharp allyl ether odor was replaced by a phenol-like odor. Purification was by vacuum distillation.

In all except one case, namely, the diallyl ether of diallylresorcinol, it was shown that both allyl groups in the diallyl ethers wandered from oxygen to a carbon of the aromatic nucleus. Every rearrangement product in the catechol series gave an intense color reaction with ferric chloride, and gave a characteristic gray precipitate with an ammoniacal solution of calcium chloride. Starting with an acetone solution of each of the catechol compounds, the lead salts were readily prepared by precipitation with lead acetate (in acetone solution, 33%).

For an analysis of the lead salts, the sample (0.2–0.5 g.) was washed first with acetone, then with water, dried to constant weight at 105° and then dissolved (pink solution) with 25 cc. of 25% acetic acid. To this, while hot, was added 3 cc. of concd. sulfuric acid in 10 cc. of water. The mixture was boiled for a short time to coagulate the lead sulfate, which was then collected and weighed.

Similarly, the rearranged products in the resorcinol series gave strong ferric chloride color reactions. The identity of each product of rearrangement was proved by analysis. Certain reactions which are mentioned below were carried out to supply evidence regarding the orientation of the allyl groups in the rearrangement. Details will be supplied only in one case, namely, the pyrolysis of the monoallyl ether of resorcinol. Others will be summarized in Table II.

TABLE II

PYROLYSIS OF ALLYL ETHERS OF CATECHOL AND RESORCINOL COMPOUNDS, TEMPERATURES AND PRODUCTS

No.	Ether heated	Temperature of rearrangement	Product
1	Catechol monoallyl	170–175°, exothermic	3-Allyl- and 4-allylcatechol
3	Catechol diallyl	180°, vig. exotherm.	3,6-Diallylcatechol
5	3-Allylcatechol monoallyl	[a]	3,6-Diallylcatechol
6	3-Allylcatechol diallyl	[a]	Triallylcatechol
8	Diallylcatechol diallyl	180–200°	Tetra-allylcatechol
10	Resorcinol monoallyl	210–220°, exotherm.	4-Allylresorcinol[b]
11	Resorcinol diallyl	210°, mod. heat ev.	4,6-Diallylresorcinol
12	Diallylresorcinol diallyl	[a]	1,3,5 - Triallyl - 2 - allyloxy-4-hydroxybenzene

[a] In these cases the original ether underwent rearrangement during its purification by vacuum distillation. [b] 1-Allyl-2,4-dihydroxybenzene.

BOILING POINTS AND ANALYTICAL DATA

No.	Boiling point °C.	Mm.	Formula	Analyses, % Calcd.	Found	
1	See Reference 2 for boiling point and analytical data					
2	(Lead salt of 1)		$C_9H_8O_2Pb$	Pb, 58.3	58.6	58.2
3	165–170	25	$C_{12}H_{14}O_2$	C, 75.8	75.76	76.15
				H, 7.57	7.43	7.57
4	(Lead salt of 3)		$C_{12}H_{12}O_2Pb$	Pb, 52.8	50.7	52.5
5	162–165	20	....	...	...	...
6	186–189	22	....	...	...	...
7	(Lead salt of 6)		$C_{15}H_{16}O_2Pb$	Pb, 47.6	48.3	48.1
8	196–200	22	....	...	...	...
9	(Lead salt of 8)		$C_{18}H_{20}O_2Pb$	Pb, 43.6	43.0	43.9
10	144–146	5	$C_9H_{10}O_2$	C, 72.0	71.5	
				H, 6.67	6.97	
11	160–163	5	$C_{12}H_{14}O_2$	C, 75.8	75.3	
				H, 7.37	7.16	
12	182–184	5	....	Analyzed as phenyl isocyanate derivative (below)		

Pyrolysis of the Monoallyl Ether of Resorcinol.—Twenty-two g. of the purified ether was placed in a flask which was heated in a salt-bath. The nature of the exothermic reaction was followed by observing the inner temperature of the flask and the outer temperature of the bath at one-minute intervals.

	Start	1 min.	2	3	4	5	6	7
Inner temp., °C.	170	180	212	280	265	260	248	246
Outer temp., °C.	200	220	226	240	245	245	245	246

The yield of 4-allylresorcinol, which boiled at 144–146° and 5 mm., was 10 g. or 45% of the theoretical.

In another experiment 40 g. of the ether was taken. At an outer temperature of 235°, the inner temperature ascended to 310° and the contents of the flask were boiling vigorously. Only 5 g. of distillate could be obtained from this. It was a very viscous, red liquid which hardened on standing. The residue in the flask solidified to an amber resin. It fused at 95–100°. This material dissolved readily in ether, acetone and 10% sodium hydroxide solution. The alkaline solution was dark red. It was also soluble in hot toluene, hot benzene and hot alcohol. When these solutions were cooled, only tarry material separated. Water, ligroin or carbon disulfide failed to dissolve it.

Quantities less than 20–25 g. should be taken to avoid this vigorous exothermic reaction which leads to tars. In addition to this precaution the heat should be removed from underneath the bath once the exothermic reaction starts.

Proof of Structure of 4-Allylresorcinol

4-Propenylresorcinol.—Four g. of the allylresorcinol, formed by pyrolyzing resorcinol monoallyl ether, was heated[8] at 180° with 5 g. of potassium hydroxide. The product was then dissolved in water and acidified. The oil was separated. It was not purified[9] but was methylated directly.

The methylation into 1-propenyl-2,4-dimethoxybenzene was conducted in the usual way with an excess of dimethyl sulfate and 30% sodium hydroxide solution. The product was oxidized directly by potassium permanganate solution which was slightly alkaline. After filtering off the manganese dioxide and subsequent concentration of the filtrate, the latter was acidified. The cloudy solution was extracted with ether. The red oil thus isolated was crystallized from hot water. Animal charcoal was used to decolorize the solution. About 0.5 g. of 2,4-dimethoxybenzoic acid, melting at 106–109°, was thus produced.

1-Allyl-2,4-dimethoxybenzene.—A portion of the 4-allylresorcinol was methylated directly by dimethyl sulfate and alkali. The allyl-2,4-dimethoxybenzene thus produced was a liquid possessing these physical properties: b. p. 82–85° at 4 mm.; n_D^{15} 1.5318; n_D^{20} 1.5294.

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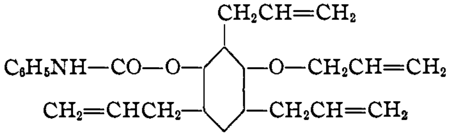
[8] A temperature of 200° was found to give rise to much tarry material.

[9] Using a similar procedure, it was demonstrated that eugenol rearranged into isoeugenol in yields of more than 60%.

Anal. Subs., 0.2664: CO_2, 0.7292; H_2O, 0.1880. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.83. Found: C, 74.4; H, 7.85.

1-Propenyl-2,4-dimethoxybenzene and its Oxidation.—As with 4-allylresorcinol, 2 g. of its dimethyl ether was heated for one hour with moistened potassium hydroxide at 160°. The propenyldimethoxybenzene was worked up as in the former case. Oxidation of this material also yielded the 2,4-dimethoxybenzoic acid. With one crystallization it melted for the most part at 104–107°; the final traces melted at 110°.

Structure of 1,3,5-Triallyl-2-allyloxy-4-hydroxybenzene.—To establish the presence of one or two free hydroxyls in the product of rearrangement of the diallyl ether of diallylresorcinol, 1 cc. of the rearranged product (b. p. (5 mm.) 182–184°) was heated with 1 cc. of phenyl isocyanate. The crystals which formed were filtered off and washed with ether. This urethan was readily soluble in hot alcohol, from which it crystallized nicely on cooling; m. p. 160–161°. Analysis revealed the presence of but one nitrogen atom per molecule of substance. Thus the formula is



Anal. (Kjeldahl). Calcd. for $C_{24}H_{27}O_3N$: N, 3.71. Found: 4.19, 3.87.

Summary

The allyl ethers of catechol and of resorcinol rearrange by heating, in a manner which is characteristic of other aryl allyl ethers. Allylcatechols and allylresorcinols are thereby formed. Allyl ethers of these substances, in turn, rearrange similarly in all cases where rearrangement is anticipated. The monoallyl ether of resorcinol gives rise to 4-allylresorcinol rather than the 2-isomer. Both allyl groups in the diallyl ether of diallylcatechol wander from the oxygen to the nucleus, and tetra-allylcatechol is formed. As would be expected, only one of the two groups in the analogous resorcinol compound undergoes a similar rearrangement.

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