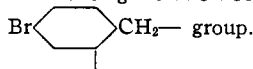


Attempts to oxidize the *p*-bromobenzyl resin with chromium trioxide, permanganate and with sodium dichromate were unsuccessful. Bromination in sunlight gave a product melting at 225–235° the analysis of which indicated one bromine atom per



Anal. Calcd. for (—C₇H₄Br₂—)_x: Br, 64.40. Found: Br, 63.20, 62.82.

Summary

1. Polymerization of benzyl chloride has been effected by small amounts of aluminum chloride, ferric chloride, and stannic chloride. Aluminum chloride yielded mainly an insoluble hydrocarbon (C₇H₆)_x and a small amount of soluble resin having the same empirical formula. The proportions of these were reversed when ferric chloride was employed, while stannic chloride yielded entirely the soluble polymer. The molecular weights of the soluble resin varied from 1260 to 2250. The hydrocarbon chains were not readily attacked by oxidizing agents.

2. Polymerization of *p*-bromobenzyl chloride has been effected under similar conditions and with comparable results. The structural unit of both the insoluble and soluble polymers was C₇H₅Br and the molecular weights of the resin varied from 1300 to 1500.

3. Polymers have been obtained from *p*-dibromobenzene and *p*-xylylene bromide by means of the Wurtz reaction. The former yielded a soluble polymer whereas the latter gave an infusible insoluble polymeric hydrocarbon having the empirical formula (C₈H₈)_x.

WILMINGTON, DELAWARE

[201ST CONTRIBUTION FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

THE CHEMISTRY OF LIGNIN. VI. THE DISTILLATION OF ALKALI LIGNIN WITH ZINC DUST IN AN ATMOSPHERE OF HYDROGEN

BY MAX PHILLIPS AND M. J. GOSS

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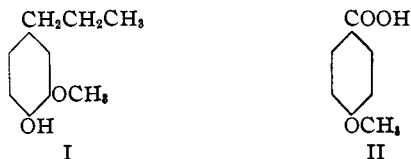
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In a previous communication by one of us¹ the results of some experiments on the distillation of lignin with zinc dust in an atmosphere of hydrogen were given. Among the products of distillation obtained were catechol, guaiacol, and a phenolic methyl ether which gave a 3,5-dinitrobenzoyl derivative melting at 110°.

The present paper gives the results of a further study of the same reaction. In addition to the degradation products mentioned above, we have succeeded in isolating a phenolic compound which has been identified as 1-*n*-propyl-3-methoxy-4-hydroxybenzene (I). When oxidized with

¹ Phillips, THIS JOURNAL, 53, 768 (1931).

aqueous potassium permanganate the "neutral fraction" of the oily distillate from the zinc dust distillation of the lignin yielded anisic acid (II).



The isolation of these two compounds as degradation products of lignin indicates that there are in the lignin molecule in addition to other possible units at least two aromatic nuclei or those which can be readily converted into aromatic nuclei. One nucleus has a side chain having at least three carbon atoms in addition to a methoxyl group and a hydroxyl group in the positions meta and para, respectively, to the side chain. The other nucleus has a side chain and a methoxyl substituent para to the side chain.

Experimental

The lignin² was distilled with zinc dust at a maximum temperature of 400° in the type of apparatus and under the conditions previously described.³ A total of 250 g. of lignin was distilled, and the yield of oil amounted to 37.5 g. (≈15% of the weight of the lignin used). The oil obtained was dissolved in ether. This solution was extracted with 5% aqueous sodium hydroxide and thus resolved into an alkali-soluble fraction and an alkali-insoluble or neutral fraction. The alkali-soluble portion was acidified and the phenolic oil was steam distilled. The residue in the distilling flask was a tarry mass from which nothing definite could be isolated. The steam volatile phenols were dissolved in an equal volume of anhydrous ether, cooled with ice, and an excess of a saturated solution of potassium hydroxide in absolute alcohol was then added. After standing for about one-half hour the potassium phenolate was filtered off and washed with anhydrous ether. The potassium phenolate was dissolved in water, acidified with sulfuric acid, and the phenol was extracted with ether. The ether solution was dried over anhydrous sodium sulfate and filtered, and after removal of the ether by distillation the oily residue was distilled. The oil distilled over at 202–207°; yield 1 g. The 3,5-dinitrobenzoyl ester of this was prepared by the method previously described.⁴ After two crystallizations from 95% ethanol, crystals were obtained melting at 114° (corr.). The melting point of the 3,5-dinitrobenzoyl ester of 1-*n*-propyl-3-methoxy-4-hydroxybenzene is 116° (corr.). The optical properties of the crystals melting at 114° were also found to be identical with those of the 3,5-dinitrobenzoyl ester of 1-*n*-propyl-3-methoxy-4-hydroxybenzene.

The filtrate from the solid potassium phenolate was acidified with dilute sulfuric acid and extracted with ether. The ether solution was dried over anhydrous sodium sulfate and filtered and, after removal of the solvent, the residual oil was fractionally distilled. The following two fractions were obtained: (1) 196–203°, 1 g.; (2) 203–215°, 2.5 g.

Fraction 196–203°.—The 3,5-dinitrobenzoyl ester of this was prepared. After three crystallizations from 95% ethanol, crystals were obtained which melted sharply

² The lignin used in these experiments was isolated from corn cobs following the method indicated in a previous communication (Ref. 1, p. 770).

³ Ref. 1, p. 770.

⁴ Phillips and Keenan, *THIS JOURNAL*, **53**, 1924 (1931).

at 141° (corr.). When this substance was mixed with some pure 3,5-dinitrobenzoyl-guaiacol, the resulting mixture also melted at 141°. The optical properties of the crystals of the two preparations were also found to be identical. This fraction, therefore, consisted principally of guaiacol.

Fraction 203–215°.—The 3,5-dinitrobenzoyl ester was prepared and after three crystallizations from 95% ethanol it melted sharply at 116.8° (corr.). When mixed with some pure 3,5-dinitrobenzoyl ester of 1-*n*-propyl-3-methoxy-4-hydroxybenzene, no depression in the melting point was observed. The optical properties of the crystals of the ester prepared from fractions 203–215° were in every respect identical with those of the 3,5-dinitrobenzoyl ester of 1-*n*-propyl-3-methoxy-4-hydroxybenzene.

Examination of the "Neutral Fraction."—The ether solution which had been extracted with 5% sodium hydroxide solution was filtered and the ether distilled off. The residue was distilled in a current of steam; the distillate and the aqueous residue in the flask were extracted with ether. Both ether solutions were dried over anhydrous sodium sulfate and filtered, and the ether was removed by evaporation. A steam volatile neutral fraction (A) and a steam non-volatile neutral fraction (B) were thus obtained. The yields amounted to 7 and 3 g., respectively.

Examination of Steam-Volatile Neutral Fraction A.—This was distilled under ordinary pressure, and two fractions were obtained, namely, 215–230° (3.0 g.) and 230–260° (2.5 g.).

Oxidation of Fraction 215–230° with Potassium Permanganate.—The oil was placed in a flask which was attached to an inverted condenser. The flask was heated in a boiling water-bath and a 4% aqueous potassium permanganate solution added with stirring until no further decoloration of the permanganate solution took place. The excess of potassium permanganate was destroyed with hydrogen peroxide; the manganese dioxide was filtered off, and the alkaline filtrate was concentrated and then acidified with hydrochloric acid, whereupon a colorless crystalline precipitate was obtained. This was crystallized from dilute alcohol and colorless needles, melting at 184° (corr.), were obtained. When a portion of this crystalline substance was mixed with some pure anisic acid, the melting point of the mixture was also 184° (corr.).

Anal. (Methoxyl). Subs., 0.0205: AgI, 0.0317. Calcd. for C₈H₈O₃; OCH₃, 20.39. Found: OCH₃, 20.43.

The optical properties of the crystals of the acid melting at 184°, obtained by the oxidation of fraction 215–230°, were also found to be identical with those of anisic acid.

Oxidation of Fraction 230–260°.—This was oxidized with aqueous potassium permanganate according to the method previously described. The concentrated filtrate from the manganese dioxide was acidified with hydrochloric acid and, as no precipitate separated out, the solution was extracted with ether, and the ether was distilled off. The residue was crystallized from dilute alcohol, from which it separated out as needles. This was identified as anisic acid by its melting point, mixed melting point and by the optical properties of the crystals.

The steam non-volatile neutral fraction (B) was distilled under reduced pressure (9 mm.). It distilled over as a viscid oil at 180–190° from which, however, nothing definite was obtained.

Distillation of Lignin with Zinc Dust at Low Red Heat.—The distillations were carried out in an ordinary electrically heated combustion furnace. The combustion tube was filled in a manner similar to that used in the previous experiment. Altogether seven runs were made representing a total of 260 g. of lignin. The oil obtained in the various runs was combined and the total amounted to 28.5 g. (≈10.9% of the weight of the lignin distilled).

A chemical examination of this oil was made according to the procedure given

above. In the phenolic fraction only guaiacol was identified. The "neutral" fraction on oxidation yielded an acid which was identified as anisic acid by its melting point, mixed melting point, and the optical properties of the crystals.

Summary

1. Alkali lignin, isolated from corn cobs, was distilled with zinc dust in an atmosphere of hydrogen at a maximum temperature of 400°. The oily distillate was separated into a phenolic fraction and a "neutral" fraction. In the phenolic fraction guaiacol and 1-*n*-propyl-3-methoxy-4-hydroxybenzene were identified. The "neutral fraction" when oxidized with potassium permanganate yielded anisic acid.

2. The significance of these findings from the standpoint of the structure of lignin is briefly discussed.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE PRIVATE LABORATORY OF THE AUTHOR]

ALKYLATION OF ORANGE I. A REFUTATION

BY KARL H. T. PFISTER

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Introduction

There has recently appeared a paper by K. H. Slotta and W. Franke,¹ entitled "Zur Konstitution der Azo-Indicatoren. I. Mitteilung: α -Naphthol-Orange" ("The Constitution of Azo Indicators. Part I. α -Naphthol Orange").

When the writer first glanced over this paper, he was struck by the novel character of it, and by the departure of the two authors from long established and often confirmed experience, concerning the constitution and certain typical properties of those azo dyes which carry a phenolic hydroxyl group in para position to the azo group. Such dyes have always been known to be very sensitive to the action of alkali, in so far as their usually yellow or orange shades are turned deep red, even by weak alkalies. It has been recognized long ago that the alkylation of the hydroxyl group renders these dyes indifferent, or to use the technical term, "fast" to alkali, and thereby makes them suitable for certain practical applications—for instance, the dyeing of textile goods.

Amongst the members of the group of azo dyes mentioned above, there is one called Alpha-Naphthol-Orange or Orange I, which is made by coupling diazotized sulfanilic acid with α -naphthol, and it is this particular dye with which the paper of Slotta and Franke deals.

It seems that relative to the alkylation of this dye, there is no reference in the chemical literature previous to the article of Slotta and Franke but

¹ Slotta and Franke, *Ber.*, 64, 86 (1931).