[A CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY][1]

Interpretation of Lignin. II. The Synthesis of Further Analogs of Spruce Lignin

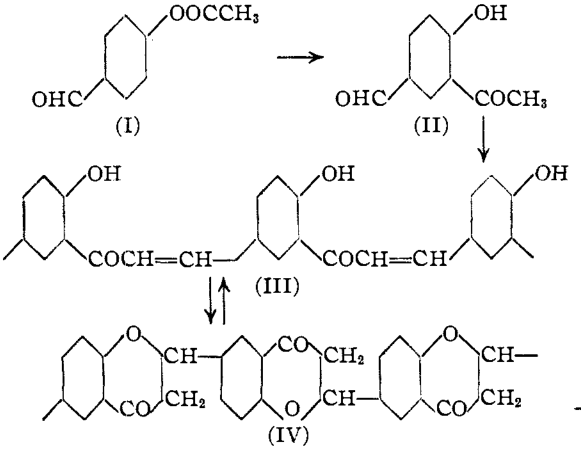
BY ALFRED RUSSELL[2]

The facile synthesis of a polymeric material having the structure proposed for spruce lignin has already been described.[3]

The product desired was shown to be available by condensation polymerization of 2-hydroxy-3-methoxy-5-formylacetophenone, the polymerization following immediately upon the formation of the ketone by Fries rearrangement of vanillin monoacetate. The methyl ketoaldehyde cannot be isolated. It undergoes polymerization, involving continued intermolecular aldolization, with loss of water, at once under the anhydrous conditions of the rearrangement reaction.

The analytical values for the polymer were not as good as are normally attainable because of the unavoidable partial demethylation of the polymer that occurs during its formation. To demonstrate the course of the polymerization satisfactorily from the point of view of simple analysis, it would be desirable either to avoid demethylation or to carry out the reaction starting with the analog of vanillin containing no methoxyl group—*p*-hydroxybenzaldehyde. The second is the more feasible of these and has been accomplished.

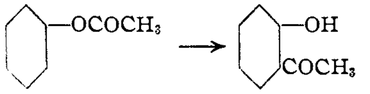
By Fries rearrangement of *p*-acetoxybenzaldehyde (I), 2-hydroxy-5-formylacetophenone (II) results and at once polymerizes to (III) and (IV). The analytical values for the polymer are in excellent agreement with those required and, upon exhaustive methylation, the methylated product gives methoxyl values corresponding to one methoxyl group for each monomeric residue.



(I) (II) (III) (IV)

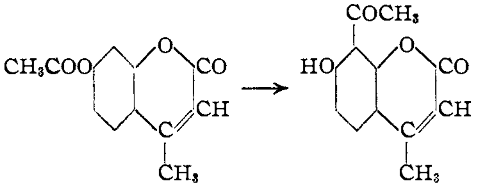
Further to explore the general course of the polymerization reaction, it was extended to the examination of the final product of Fries rearrangement of salicylaldehyde monoacetate. In this case it is possible to predict with some accuracy the position occupied by the acetyl group after rearrangement.

Rearrangement of phenyl acetate gives chiefly *o*-hydroxyacetophenone (V) → (VI). Indeed, this is the best method for preparing the ketone.



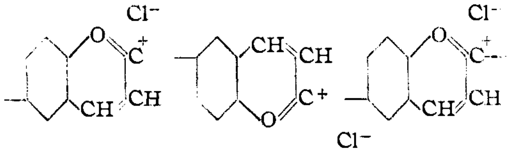
(V) (VI)

Some of the *p*-isomer is, of course, obtained simultaneously. Rearrangement of 4-methyl-7-acetoxycoumarin (VII) gives 4-methyl-7-hydroxy-8-acetylcoumarin (VIII) *exclusively* since removal of the coumarin ring is easily effected with warm dilute alkali, giving only 2,6-dihydroxyacetophenone. In this case, the labilized acetyl group assumes a position in the ring *meta* to the carbon side chain and *ortho* to *both* the hydroxyl group and to the bridge oxygen of the coumarin ring. In the case of salicylaldehyde monoacetate, then, the rearrangement product should be mostly, or even entirely, 2-hydroxy-3-formylacetophenone rather than 4-hydroxy-5-formylacetophenone.

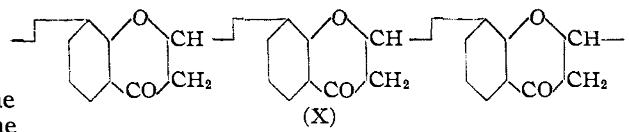


(VII) (VIII)

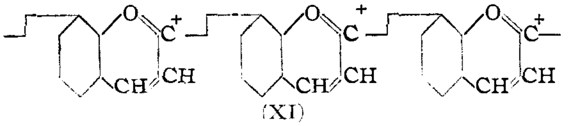
Therefore, the polymer cannot be the polybenzopyrilium salt (IX) but must be either the polydihydrobenzopyrone (X) or the polybenzopyrilium salt (XI).



(IX)



(X)



(XI)

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] Deceased June 28, 1948.

[3] A. Russell, THIS JOURNAL, **70**, 1060 (1948).

The polymeric product is light (flesh) in color; a benzopyrilium salt of this kind would be very dark in color (purple, dark maroon or black). Moreover, it contains no halogen and must therefore have the structure (X). This result is rather unexpected if the ease of ring closure of 2-hydroxychalcones to flavilium salts and the difficulty of ring closure of 2′-hydroxychalcones to flavanones are recalled by way of analogy.

It is understood, of course, that analogs of lignin having the same polymeric structure as (IV) may well occur naturally. It is also possible, but not nearly so probable, that polymers having the same structure as (X) may be found.

Experimental

Fries Rearrangement of *p*-Acetoxybenzaldehyde.—*p*-Acetoxybenzaldehyde (10 g., 1 mol.) was dissolved in dry nitrobenzene (50 g.) and anhydrous aluminum chloride (18 g., 2 moles) added portionwise, with shaking, over five minutes. The reaction mixture was heated to 110–120° for ninety minutes, cooled and decomposed with dilute hydrochloric acid (200 cc., 5%). The nitrobenzene was removed by steam distillation and the light brown, amorphous reaction product collected. It was difficultly, or only very slightly if at all, soluble in ethanol, acetone and dioxane; totally insoluble in ether, hydrocarbons, and halogenated solvents. Finally, for purification, it was dissolved in dilute (1 to 2%) alkali and reprecipitated by filtering into ice cold dilute (*ca.* 3%) hydrochloric acid. After several reprecipitations the pink, near gelatinous, material was collected, washed with water until free of acid, and dried completely (twenty days, 23 mm., potassium hydroxide). As anticipated, the wet material was easily soluble in sodium bisulfite solution (*ca.* 10%), the dried material much less so, and the solubility diminished as aging proceeded.

Anal.[4] Calcd. for $(C_9H_6O_2)_n$: C, 74.0; H, 4.11. Found: C, 74.2, 73.7; H, 4.6, 4.5.

Methylation of 2,6-Polydihydrobenzopyrone.—2,6-Polydihydrobenzopyrone (2 g.) was dissolved in 10% aqueous sodium hydroxide (40 cc.). At the temperature of the steam-bath, dimethyl sulfate (12 g.) was added portionwise with shaking. Then, with heating and shaking, a further quantity of dimethyl sulfate (24 g.) was added in portions and the reaction mixture kept alkaline by addition of portions of 20% aqueous sodium hydroxide as needed. Finally the alkali insoluble reaction product was collected, washed, and dried.

Anal. Calcd. for $(C_9H_5O.OCH_3)_n$: "OCH_3," 19.37. Found: "OCH_3," 19.8, 20.1.

Fries Rearrangement of Salicylaldehyde Monoacetate.—Salicylaldehyde monoacetate (12.3 g., 1 mol.) was dissolved in dry nitrobenzene (75 cc.) and anhydrous aluminum chloride (20.2 g., 2 mol.) added portionwise, with occasional shaking, over ten minutes. The reaction mixture was held at 120° for an hour, cooled and decomposed with ice cold dilute hydrochloric acid (400 cc., 3%). After removal of the nitrobenzene by steam distillation, the light (flesh) colored solid was collected, washed with water until free of acid, and reprecipitated three times with water from solution in acetone. After drying, it formed a fawn-colored amorphous solid, somewhat soluble in acetone, rather insoluble in ethanol and dioxane, and insoluble in hydrocarbon and halogenated solvents. It showed the same solubility characteristics in aqueous sodium bisulfite as the analogous polymers already described.

Anal. Calcd. for $(C_9H_6O_2)_n$: C, 74.00; H, 4.11. $C_9H_8O_3$: C, 65.9; H, 4.87. Found: C, 71.0, 71.2; H, 4.57, 4.59.

Summary

The polymerization reaction used in the synthesis from vanillin of a polymeric material having the structure proposed for spruce lignin has been extended to the preparation of analogous polymeric materials from *o*- and *p*-hydroxybenzaldehydes.

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[4] Analyses are microdeterminations by C. H. Van Etten and Mary B. Wiele of this Laboratory.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF TRINITY COLLEGE AND NORTHWESTERN UNIVERSITY]

Catalytic Racemization and Dehydrogenation of Optically Active Secondary-butyl Alcohol by Copper and by Zinc Chromite

BY ROBERT L. BURWELL, JR.

Optically active *s*-butyl alcohol is both racemized and decomposed in passage over certain catalysts.[1] Copper gives pure dehydrogenation and a distinctly smaller ratio of racemization to decomposition than that found with other catalysts. Zinc chromite exhibits dehydrogenation accompanied by a small amount of condensation and a large amount of racemization. It could not be decided, particularly for copper, whether racemization resulted solely from inactive alcohol produced by hydrogenation of the dehydrogenation product, methyl ethyl ketone.

Dehydrogenation of alcohols by copper was extensively investigated in the classical work of Palmer and Constable[2,3,4] though this work was largely confined to primary alcohols. Certain kinetic data dealing with the dehydrogenation of secondary alcohols by copper do, however, exist: isopropyl alcohol,[3,5,6] *s*-butyl alcohol,[6,7] cyclohexyl alcohol,[3,5] and 2-octanol.[6]

Analogous kinetic studies with zinc chromite have not been reported but this substance has

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[1] Burwell, THIS JOURNAL, **59**, 1609 (1937).

[2] Palmer, *Proc. Roy. Soc.* (*London*), **98A**, 13 (1920).

[3] Palmer and Constable, *ibid.*, **107A**, 255 (1925).

[4] Constable, *ibid.*, **107A**, 279 (1925).

[5] Balandin, Marushkin and Ikonnikov, *Uchenye Zapiski Moskov. Ordena Lenina Gosudarst. Univ. im. M. V. Lomonosova*, **2**, 221 (1934); *Chem. Centr.*, **106**, II, 1528 (1935).

[6] Neish, *Can. J. Research*, **23B**, 49 (1945).

[7] Balandin and Liberman, *Compt. rend. acad. sci. U. R. S. S.*, **28**, 794 (1940).