cyclopentane, and differ appreciably from those of the four known chloroperfluoromethylcyclohexanes.[10]

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## Summary

The condensation of hexachlorocyclopentadiene with trichloroethylene in the presence of aluminum chloride produces 5-(1,2,2,2-tetrachloroethyl)-pentachlorocyclopentadiene, which undergoes dehydrohalogenation with aluminum chloride and alkali to form two isomeric chlorocarbons, $C_7Cl_8$, octachloro-1 or 2-vinylcyclopentadiene and octachloro-5-ethylidenecyclopentadiene, respectively. The former chlorocarbon was identified by its conversion to the unsaturated derivatives of ethylcyclopentane, $C_7ClF_{11}$ and $C_7Cl_2F_{10}$, chlorotridecafluoroethylcyclopentane, hexachloro-5,5-dimethoxy-1 or 2-vinylcyclopentadiene, hexachloro-2 or 3-vinylcyclopentadiene, hexachloro-2 or 3-vinylcyclopentadienone and its Diels–Alder dimer, and hexachlorovinylcyclopentenedione. The latter chlorocarbon was identified by its conversion to pentachlorocyclopentadienylideneacetyl chloride and functional derivatives thereof.

Whereas hexachlorocyclopentadiene readily undergoes the Diels–Alder reaction and also forms a dimer in the presence of aluminum chloride, the isomeric chlorocarbons $C_7Cl_8$ do not react with maleic anhydride under ordinary conditions. On the other hand, hexachloro-2 or 3-vinylcyclopentadienone dimerizes spontaneously via Diels–Alder.

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[10] B. W. Hotten, Ph.D. Dissertation, Purdue University, 1945; J. Davis, Ph.D. Dissertation, 1947.

[11] Original manuscript received May 17, 1948.

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[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY, PEORIA, ILLINOIS[1]]

# Interpretation of Lignin. III. The Synthesis and Polymerization of Stable Monomers[2]

BY ALFRED RUSSELL,[3] JOHN H. BAITY[4] AND HERBERT E. SMITH

There have already been described syntheses of three polymeric materials; one of these had many of the properties of spruce lignin[5] and the others were methoxyl-free analogs.[6] The polymers resulted by chain-like intermolecular aldolization of certain aryl methylketoaldehydes. The monomeric units were prepared by the Fries rearrangement of the monoacetates of monohydroxyarylaldehydes and could not be isolated due to their reactivity under the anhydrous conditions of the rearrangement reaction—polymerization proceeding at once to give polydihydrobenzopyrones.

It would be of interest to demonstrate the existence of similar stable monomeric units and their separate polymerization. Such methylketoaldehydes should be available by two general methods, either nuclear acylation of *suitably chosen* hydroxyarylaldehydes or nuclear formylation of *suitably chosen* hydroxyaryl ketones. Inactivation of the carbonyl group in the initial material by any conventional method would most likely be ineffective because the acylated or formylated reaction product would likely polymerize as soon as the inactivated carbonyl group was liberated if it did not do so even before liberation of the protected group.

A much more elegant procedure is to prepare a monomer which, because of its configuration, cannot polymerize easily. This may be accomplished by selecting the starting material so that the carbonyl group already present is chelated with an hydroxyl group and the second carbonyl group enters ortho to another hydroxyl group. A second chelate ring will form at once and, at least in some cases, the monomer should be stable.

Six such schemes may be tried rather easily since the starting materials are accessible: the nuclear acylation of β-resorcylaldehyde or of pyrogallic aldehyde; the nuclear formylation of resacetophenone, 2,6-dihydroxyacetophenone, gallacetophenone and 2,4,6-trihydroxyacetophenone (phloracetophenone).

No success was had in acylation attempts and the application of the Gattermann procedure to gallacetophenone was equally futile. However, the formylation of the other three hydroxy ketones by the Gattermann procedure, modified in one instance, was entirely successful and satisfactory yields were obtained of the three methylketoaldehydes — 2,4 - dihydroxy - 3 - formylacetophenone, 2,6-dihydroxy-3-formylacetophenone and 2,4,6-trihydroxy-3-formylacetophenone. All three monomers are stable, easily crystalline with sharp melting points. All three are unchanged by 40% aqueous alkali and by 50% sodium methoxide in methanol, but may be polymerized to red or brown amorphous materials by

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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.

[2] Article not copyrighted.

[3] Deceased.

[4] Former Employee, Industrial Chemical Section, Agricultural Residues Division.

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

[6] A. Russell, *ibid.*, **70**, 2864 (1948).

sufficiently strong alcoholic sulfuric acid. The polymers are inert alkali-soluble materials and have similar solubility characteristics in organic solvents to those previously described. Some part of the polymer from the trihydroxy compound is slightly water-soluble.

Although each ketoaldehyde has a more or less reactive nuclear position, it does not seem likely that the polymers are phenol–aldehyde condensation products because of steric effects. They are not polybenzopyrrilium salts for they contain no halogen after reprecipitation from alkaline solution with hydrochloric acid. They may be formulated as in previous cases.

## Experimental

**Polymerization of 2,4-Dihydroxy-3-formylacetophenone[7] to Poly(2,8)-7-Hydroxydihydrobenzopyrone.**—2,4-Dihydroxy-3-formylacetophenone (1 g.) was dissolved in ethanol (20 cc.) and concentrated sulfuric acid (7.5 cc.) added. The whole was refluxed for thirty minutes, cooled and the deep red reaction mixture poured into water (250 cc.). The red amorphous precipitate was collected and washed free from acid. It was dissolved in dilute sodium hydroxide (100 cc., 5%) and reprecipitated with ice-cold hydrochloric acid. It was collected, washed free from acid and divided empirically into two fractions: (1) ether-dioxane insoluble, (2) dioxane–water insoluble.

*Anal.*[8] Calcd. for $C_9H_8O_4$: C, 60.44; H, 4.44. $C_9H_6O_3$: C, 68.66; H, 4.94. Found for $C_9H_8O_4$: C, 64.4, 64.7; H, 4.86, 4.80. $C_9H_6O_3$: C, 66.5, 66.3; H, 4.84, 4.83.

**Formylation of 2,6-Dihydroxyacetophenone.**—2,6-Dihydroxyacetophenone[9] (15 g. 1 mol) was dissolved in anhydrous ether (250 cc.) and dry, freshly prepared zinc cyanide (23 g., 2 mol) added. Anhydrous hydrogen chloride was passed into the ice-cold solution to saturation (six to seven hours). The reaction mixture was allowed to stand overnight (sixteen hours) and the supernatant ether poured away from the dark brown oil which was washed twice with 50-cc. portions of dry ether. The washed oil was treated with water (200 cc.) and traces of ether evaporated. Upon steam distillation, 2,6-dihydroxy-3-formylacetophenone was collected as a colorless solid. Recrystallized from dilute ethanol it forms colorless needles m. p. 101–102°; yield, 6.2 g.

*Anal.* Calcd. for $C_9H_8O_4$: C, 60.00; H, 4.44. Found: C, 60.1, 59.8; H, 4.19, 4.13.

**Polymerization of 2,6-Dihydroxy-3-formylacetophenone to Poly-(2,6)-5-Hydroxydihydrobenzopyrone.**—2,6-Dihydroxy-3-formylacetophenone (2 g.) was dissolved in ethanol (20 cc.) and alcoholic sulfuric acid (20 cc., 50%) added. The whole was refluxed for thirty minutes, cooled and poured into cold water. The precipitated amorphous brown solid was collected, dissolved in dilute sodium hydroxide (*ca.* 5%) and reprecipitated with ice-cold aqueous hydrochloric acid. The finely divided amorphous brown solid was collected, washed free from acid and dried.

*Anal.* Calcd. for $C_9H_8O_4$: C, 60.00; H, 4.44. $C_9H_6O_3$: C, 66.66; H, 3.70. Found: C, 64.1, 64.0; H, 4.29. 4.47.

**2,4,6-Trihydroxy-3-formylacetophenone.**—Phloracetophenone (8.4 g., 1 mol) was dissolved in anhydrous ether (125 cc.) and dry zinc cyanide (12 g., 2 mols) added, followed by anhydrous aluminum chloride (13 g., 1 mol) dissolved in anhydrous ether (50 cc.). The reaction mixture was cooled in Dry Ice and saturated with dry hydrogen chloride (seven hours). An orange-yellow colored solid started to separate after about two hours. Separation was completed by allowing to stand overnight. The supernatant ether was poured away and the residue washed twice with 50-cc. portions of dry ether. Water (125 cc.) was added to the solid residue and traces of ether evaporated. Upon raising the temperature the reaction product dissolved and a yellowish-colored crystalline precipitate separated. The whole was cooled, the solid product collected and recrystallized from dilute ethanol (charcoal). 2,4,6-Trihydroxy-3-formylacetophenone forms pale yellow microcrystalline needles m. p. 176°. The yield was 7.1 g. (73%).

*Anal.* Calcd. for $C_9H_8O_5 \cdot H_2O$: C, 50.5; H, 4.7. Found: C, 50.8, 51.0, 50.5; H, 4.97, 4.84, 4.42.

**Polymerization of 2,4,6-Trihydroxy-3-formylacetophenone.**—2,4,6-Trihydroxy-3-formylacetophenone (2 g.) was dissolved in ethanol (20 cc.) and alcoholic sulfuric acid (20 cc., 50%) added. The whole was refluxed for thirty minutes, cooled and poured into water (200 cc.). The bright red flocculent precipitate was collected, dissolved in aqueous sodium hydroxide (*ca.* 5%) and reprecipitated by dilute aqueous hydrochloric acid. The bright red amorphous precipitate was collected, washed until free from acid and dried.

*Anal.* Calcd. for $C_9H_8O_5$: C, 55.10; H, 4.08. $C_9H_6O_4$: C, 60.7; H, 3.37. Found: C, 63.7, 62.8; H, 4.42, 4.20.

## Summary

To investigate further the polymerization reaction used in the synthesis of lignin-like materials, three stabilized monomeric units—2,4-dihydroxy-3-formylacetophenone, 2,6-dihydroxy-3-formylacetophenone and 2,4,6-trihydroxy-3-formylacetophenone have been prepared, and separately polymerized.

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(7) Shah and Shah, *J. Chem. Soc.*, **132** (1939).

(8) All analyses are microdeterminations by Mr. G. H. Van Etten and Mrs. M. B. Wiele of the laboratory.

(9) Russell and Frye, *Org. Syn.*, **22**, 81 (1941).