NOTES

Structure of Lignin

By A. B. Cramer, M. J. Hunter and Harold Hibbert

The authors have been able to isolate recently, from spruce wood, by organic solvent extraction, an aromatic ketone in high yield (about 1–2% calculated on the weight of wood taken). This ketone is an oil, distilling at a bath temperature of 140–150° (0.004 mm.). On methylation it yields a well-defined white crystalline compound, formula $C_{13}H_{18}O_4$, m. p. 81–82°. The ketone structure of the latter product was proved by its additive power for the Grignard reagent and ready formation of a hydrazone. It also contains the veratryl radical since it gives veratric acid on oxidation.

Analysis of the methylated ketone.—Calcd. for $C_{13}H_{18}O_4$: C, 65.5; H, 7.6. Found: C, 65.5; H, 7.7. Total alkoxyl found (calculated as methoxyl): 38.7%. *Grignard machine analysis:* Addition, 0.85 mole per mole weight. Active hydrogen, 0.13 mole per mole weight.

The substance from which this crystalline product apparently is derived may be one of several isomers, each consisting of a guaiacyl group with a side chain of three carbon atoms containing a carbonyl and a hydroxyl group. The syntheses of the possible methylated compounds are now in progress. The extraordinary chemical reactivity of this type of parent substance would explain the previous difficulties associated with its isolation and characterization. Such a structure provides a satisfactory basis for interpreting the results obtained in the hydrogenation of methanol lignin at high temperatures and pressures [This Journal, **60**, 1467 (1938)].

The isolated ketone is accompanied by considerable quantities of what appears to be a polymerized product, an aldehyde, an acid, a neutral substance, and a carbohydrate-containing fraction. The combined yield of all of these products calculated on the weight of the wood taken amounts to a total of 5% in the case of spruce, and roughly 10% in the case of maple.

Work now in progress on oils from hard woods indicates the additional presence of derivatives containing the syringyl group and it is possible that this may be the fundamental chemical difference between soft and hard woods.

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The Preparation of Amyl Salicylates

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A search of the literature discloses that, of the eight theoretically possible amyl salicylates, only the normal amyl[1] and the isoamyl ester[1,2] have their properties recorded. The procedure for the preparation of the latter has been given,[2] but no reference is made to the mode of formation of the former.

In the present communication methods of preparing primary normal amyl salicylate, secondary normal amyl salicylate, and tertiary amyl salicylate are described. Isoamyl salicylate from carefully purified isoamyl alcohol and salicylic acid also has been prepared, and its physical properties have been found to be identical with those recorded by Drion.[2]

The salicylates derived from the primary amyl alcohols were prepared with sulfuric acid as the esterifying agent, but when this procedure was applied to the secondary and tertiary amyl alcohols, dehydration of the alcohol occurred, and the yield of ester was negligible. It was found, however, that the secondary and tertiary esters could be obtained on condensation of salicylic acid chloride and the carbinol in the presence of a small quantity of anhydrous aluminum chloride. With the secondary carbinol this procedure gave satisfactory yields of ester, but with the tertiary carbinol the yield of ester was small.

Primary Normal Amyl Salicylate.—A commercial grade of primary amyl alcohol was purified by fractional distillation in a column of the type described by Dupont[3] and modified by Palkin.[4] The fraction employed in the esterification had the properties: b. p. 82–83.6° at 85 mm., $n^{20}\text{D}$ 1.4109, $n^{26}\text{D}$ 1.4090, d_{20} 0.8179, $[M]\text{D}$ found 26.66, calcd. 26.815.

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(1) "International Critical Tables," Vol. I, McGraw-Hill Book Co., Inc., New York, 1926, p. 246.

(2) C. Drion, *Compt. rend.*, **39**, 122 (1854).

(3) G. Dupont, "Les Essences de Térébenthine," Paris, 1926, p. 57.

(4) S. Palkin, *U. S. Dept. Agr.*, *Tech. Bull.*, **276** (1932); *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 377 (1931); **7**, 436 (1935).

A mixture of salicylic acid (50 g.), primary normal amyl alcohol (200 g.), and concentrated sulfuric acid (2 cc.) was heated under a reflux condenser for about four hours. The apparatus was provided with a trap to remove the water that was formed. After the unreacted alcohol had been removed by distillation at atmospheric pressure, the residue was washed with 10% potassium carbonate and dissolved in ether, and the ether solution was dried over anhydrous sodium sulfate. The high-boiling material remaining after the removal of the ether was fractionated under reduced pressure by means of a Widmer column. The fraction that boiled at 116–121° and 1.4 mm. pressure was collected. The yield was 64 g.: $n^{27}\mathrm{D}$ 1.5042, d_{27} 1.0552, $[M]\mathrm{D}$ found 58.40, calcd. 58.30.

Anal.[5] Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.87. Found: C, 69.15; H, 7.82.

In all these experiments some ether was formed, the amount increasing with the time of refluxing the reaction mixtures.

Secondary Normal Amyl Salicylate.—The methyl-*n*-propylcarbinol employed in this experiment was obtained by fractional distillation of a commercial grade of the carbinol in a Dupont–Palkin[4] type of still. The purified carbinol had the properties: b. p. 61.8–64.7° at 85 mm., $n^{25}\mathrm{D}$ 1.4065, d_{25} 0.8041, $[M]\mathrm{D}$ found 26.91, calcd. 26.815.

A mixture of 40 g. of salicylic acid, 50 cc. of thionyl chloride, and 0.08 g. of anhydrous aluminum chloride was heated under reflux in a water-bath maintained at 40–50° until the acid was entirely dissolved. The solution was then concentrated at reduced pressure to remove hydrogen chloride and excess thionyl chloride. One-half of the residue, a clear, greenish-yellow liquid, was transferred to a 125-cc. Erlenmeyer flask, and 30 cc. of methyl-*n*-propylcarbinol was added in small portions. The mixture was cooled in an ice-bath for several hours, and then, with the flask stoppered with a calcium chloride tube, allowed to stand for twenty-four hours. The solution was washed several times with ice water, then with a small quantity of dilute sodium bicarbonate, and again several times with ice water. The material was dried in ether over anhydrous sodium sulfate and, after removal of the ether, was purified by repeated distillation under reduced pressure. The yield was 9.8 g. The ester boiled at 107–110° and 4–5 mm.: $n^{25}\mathrm{D}$ 1.5020, d_{25} 1.0470, $[M]\mathrm{D}$ found 58.60, calcd. 58.30.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.87. Found: C, 69.16; H, 7.81.

Tertiary Amyl Salicylate.—The tertiary amyl alcohol was a commercial grade which boiled at 100–102°. To the remaining half of the salicyl chloride prepared from 40 g. of salicylic acid by the procedure described above, 125 cc. of tertiary amyl alcohol was added slowly with vigorous shaking, the flask being kept cold in an ice-bath. Considerable hydrogen chloride was given off and some heat was evolved during the process. After standing in the ice-bath for several hours, the solution deposited a small quantity of crystalline material. This was removed by filtration, and the filtrate was distilled under reduced pressure. The pure ester was obtained by fractional distillation under reduced pressure. The yield was 6.5 g. It boiled at 84–86° and 3 mm. pressure: $n^{25}\mathrm{D}$ 1.5064, d_{25} 1.0533, $[M]\mathrm{D}$ found 58.74, calcd., 58.30.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.87. Found: C, 69.12; H, 7.88.

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Reactions of Fluorinated Derivatives with Sodium, Potassium and Magnesium

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Stable fluorinated compounds have been subjected to the action of magnesium in the hope of obtaining a Grignard reaction, and of sodium in the hope of obtaining a Wurtz reaction. In both cases the action was immediate and complete but the results were entirely different from those hoped for. The vigorous character and completeness of the reactions showed the futility of further work in the same direction and, therefore, the unexpected results are presented for publication. Some of these results (representative of what happens in other cases) were as follows.

(1) CHF_2CH_2I was dissolved in ether and allowed to drip onto clean magnesium. A reaction took place instantly. A small portion gave a faint test with Michler's ketone, indicating the formation of a Grignard compound; however, after a short period, the Grignard test was no longer positive. As the addition of CHF_2CH_2I to the magnesium was continued, a gas was evolved which was caught in bromine. It was observed that the reaction of this gas with bromine took place in the vapor phase, not the liquid, and the absorption was therefore incomplete. The gas was vinyl fluoride, as shown by the facts that the dibromide $CHFBrCH_2Br$ was the only compound found and that it was quite pure. Due to faulty experimental conditions only 50% of the vinyl fluoride was recovered as dibromide. The resulting magnesium salt was an equimolecular mixture of magnesium iodide and magnesium fluoride. Both salts are soluble in ether and in water, the fluoride as a colloid, and on account of this, a test for fluorine fails to give positive results before the magnesium fluoride has been brought from the colloidal to the crystalline stage.

(2) Attempts to cause CHF_2CH_2Br to act upon magnesium were unsuccessful.

(3) A piece of sodium or potassium reacted

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(5) We are indebted to Dr. W. G. Rose for the microcombustions.