NOTES

Structure of Lignin

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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}_{D} 1.4109, n^{26}_{D} 1.4090, d_{20} 0.8179, $[M]_{\mathrm{D}}$ 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.

energetically with CHF_2CH_2Br or CHF_2CH_2I. The reaction was run in ethyl ether, where it still was very vigorous and complete. Instead of acting upon the iodine atom only, the alkali metal removed one atom of fluorine and one atom of iodine, and gave a quantitative yield of sodium fluoride and sodium iodide or bromide. In doing so it behaved like magnesium or zinc.

(4) In contrast with the preceding result, fluorinated derivatives of methane (namely, CCl_2F_2, $CHClF_2$ and $CHBrF_2$) remained unaffected when passed through molten sodium.

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Preparation of Methylaluminum Chlorides

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The methyl- and ethylaluminum chlorides have not been reported in the literature until recently. Walker and Willson[1] showed that methyl chloride reacts with aluminum metal when catalyzed by iodine or aluminum chloride, forming an unidentified product which "may be expressed" as Me_2AlCl plus $MeAlCl_2$. Hall and Nash[2] isolated the ethylaluminum chlorides from the products of polymerization of ethylene with a mixture of aluminum and aluminum chloride, and identified the double salt $EtAlCl_2 \cdot NaCl$. Later, Grosse[3] reported the melting and boiling points of the four methyl- and ethylaluminum chlorides.

Since none of these articles gives a satisfactory method of preparation of the compounds in question, it seems desirable to describe briefly the simple method which has been used successfully in these Laboratories since some time prior to the appearance of the articles cited. This description pertains primarily to the methyl chlorides; the ethyl chlorides and the methyl and ethyl bromides have been prepared similarly.

The desired amount of aluminum metal, preferably in an alloy such as Aluminum Company of America Alloy 12 (8% copper), is cut in clean, dry shavings or chips. These are placed in a glass or steel reaction vessel equipped with: halide inlet and product discharge lines, temperature and pressure gages, provision for heating and cooling, and a safety blow-out. The catalyst, about 0.1% of anhydrous aluminum chloride (or iodine, or the product of a previous preparation) is placed in one spot on top of the aluminum, and the reaction vessel closed. Air is pumped or flushed out, and methyl chloride gas introduced to a pressure of one atmosphere (or more, depending on the equipment used). If the reaction fails to start in one hour at room temperature, the charge is heated to 100°. Once started, the reaction is autocatalytic and highly exothermic. More methyl chloride is added, and cooling is applied, at such rates as to maintain a suitable rate of reaction and to keep the temperature of the charge below 75°. At higher temperatures, side reactions may occur with the formation of gas.

When no more methyl chloride is absorbed, the reaction is completed. The reaction of the aluminum is quantitative, while any iron or copper in the alloy remains unattacked. Side reactions are negligible. In a typical preparation, about 60 millimoles of aluminum in the form of alloy took up 88.9 millimoles of methyl chloride with the formation of only 0.9 millimole of methane; the nonvolatile residue contained no aluminum and 0.4 milliatom of chlorine; no iron or copper was detected in the distilled product.

The water-white, oily liquid is decanted or vacuum distilled, from the remaining metallic sludge, into a suitable closed container. If desired, this product can be diluted with methyl chloride to lower its viscosity and to facilitate the removal of samples from the container. Such methyl chloride solutions apparently are stable in glass or steel containers, and react slowly with copper or lead. The stability of solutions of the bromides and of the corresponding ethyl compounds is less assured, and is under investigation. In any case, a safety blow-out for the container is recommended. These aluminum compounds are, of course, highly reactive toward air, moisture, and other oxygen compounds; however, their oxidation or inflammation in air is not violent.

The product of the methyl chloride reaction is almost exactly an equimolecular mixture of dimethylaluminum chloride and methylaluminum dichloride. No evidence of either trimethylaluminum or of aluminum chloride is obtained on fractional distillation. Analysis is effected by hydrolysis of a sample with wet ether followed by dilute nitric acid, and determination of the amount of methane evolved, and of the aluminum and chloride content of the solution. In a typical preparation, this analysis gave 13.58 milliatoms of aluminum, 19.60 of chlorine, and 20.46 millimoles of methane, or a ratio of Me:Al:Cl of 1.507:1:1.443.

When the individual compounds are desired, they may be separated from their mixture by fractional vacuum distillation, or the dimethylaluminum chloride may be obtained in pure form by heating the mixture with excess sodium chloride and distilling the dimethyl compound from the monomethyl addition compound. Analysis of a typical distillate from the latter procedure gave 23.4 milliatoms of aluminum, 23.6 of chlorine, and 47.1 millimoles of methane, or a ratio of Me:Al:Cl of 2.01:1:1.01.

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(1) W. O. Walker and K. S. Willson, *Refrig. Eng.*, **34**, 89, 126 (1937).

(2) F. C. Hall and A. W. Nash, *J. Inst. Petroleum Tech.*, **23**, 679 (1937).

(3) Abstracts, American Chemical Society, Dallas Meeting, 1938.