C, 64.02; H, 4.93. The percentage of acetyl groups was determined by the method of Phillips.[5] Calcd. for $C_{11}H_{10}O_4$: acetyl, 20.85. Found: acetyl, 21.30.

Acid Hydrolysis of 3-Acetoxy-6-methoxybenzofuran.—A solution of 0.5 g. of 3-acetoxy-6-methoxybenzofuran and 2 drops of concentrated sulfuric acid in 15 cc. of absolute ethanol was allowed to stand for three days with intermittent heating to boiling (3 times). At the end of this time, the solution was allowed to evaporate at room temperature until 0.2 g. of a crystalline substance was deposited. This substance melted at 108–110° but upon being recrystallized three times from ethanol melted at 118–119° and a mixed melting point with an authentic sample of 6-methoxycoumaran-3-one showed no depression.

Reduction of 3-Acetoxy-6-methoxybenzofuran.—A solution of 22 g. of 3-acetoxy-6-methoxybenzofuran in 70 cc. of absolute ethanol at 25° was reduced with hydrogen at a pressure of 2 to 3 atmospheres in the presence of 0.1 g. of platinum oxide catalyst. One mole of hydrogen was absorbed in two hours; the reduction mixture was then filtered and the solvent removed by distillation. The liquid residue distilled at 112° (10 mm.), but redistillation gave a main fraction boiling at 99–100° (10 mm.) with an appreciable forerun. The forerun proved to be mostly acetic acid and the main fraction proved to be 6-methoxybenzofuran which when purified by a third distillation gave the following constants: b. p. 99–100° (10 mm.), n^{25}_{D} 1.5620, d^{20}_{20} 1.1463; M_D calcd., 41.88; found, 41.76.

Anal. Calcd. for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 72.53; H, 5.65.

The 6-methoxybenzofuran was further characterized as the picric acid addition compound which was prepared by allowing equimolar quantities of picric acid and 6-methoxybenzofuran to combine in alcoholic solution. Partial evaporation of the solvent at room temperature deposited the addition compound in large yellow needles which when recrystallized by taking up in alcohol and partially evaporating at room temperature gave yellow needles which melted at 64–65°, which is in agreement with the melting point given by Stoermer.[7]

A few drops of the forerun was treated on a watch glass with piperazine hexahydrate[6] and the salt which formed was recrystallized from *n*-butanol to give fine white needles which melted at 208°. A mixed melting point of this substance with an authentic sample of piperazonium diacetate showed no depression.

Test for the Enol Form of 6-Methoxycoumaran-3-one.—A dilute solution of 6-methoxycoumaran-3-one in 95% ethanol was treated with a few drops of 2% ferric chloride solution. The resulting solution was indistinguishable in color from a control solution until two hours had passed, when it appeared to be assuming a red tint. At the end of twelve hours the color had changed to deep red showing slow formation of the enol form.

Summary

Acetylation of 6-methoxycoumaran-3-one with acetic anhydride gave the acetyl derivative of the enol form. That this compound was the O-acetyl derivative was shown (a) by acid hydrolysis to regenerate the parent coumaranone and (b) by catalytic reduction to 3-acetoxy-6-methoxydihydrobenzofuran which lost acetic acid to produce 6-methoxybenzofuran.

URBANA, ILLINOIS RECEIVED MARCH 18, 1938

[CONTRIBUTION FROM THE EXPERIMENT STATION, HERCULES POWDER COMPANY]

The Resin Acids. The Action of Palladium on Abietic Acid

BY EDWIN R. LITTMANN

The recent publication of Fieser and Campbell[1] on dehydroabietic acid made it desirable to present our work on the behavior of abietic acid when treated with palladium. The action of palladium at high temperatures has been reported by Fleck and Palkin[2] and by the author,[3] and the present note discusses the preparation of the dehydroabietic acid of Fieser and Campbell by a different method and presents additional evidence on the disproportionation of abietic acid.

Investigations in this Laboratory on the action of a palladium catalyst on abietic acid and methyl abietate led to the isolation of dehydroabietic acid and its methyl ester which compounds appear to be identical with those reported by Fieser and Campbell and an acid which is probably tetrahydroabietic.

When methyl abietate was passed over a palladium catalyst, supported on activated alumina, at 230°, there was obtained on cooling a pasty mass of crystals which, after filtration, washing with methanol, and recrystallization from the same solvent, could be nitrated to give a dinitro derivative, corresponding by analysis to an ester of a dinitro acid of the dehydroabietic series. This nitro derivative was stable at its melting point and gave no tests for aliphatic nitro groups with aqueous alkali or sodium ethylate. On catalytic reduction in methanol solution over copper chromite, a diamino compound was obtained which could be diazotized

---

[1] Fieser and Campbell, THIS JOURNAL, 60, 159 (1938).

[2] Fleck and Palkin, *ibid.*, 59, 1593 (1937); 60, 921 (1938).

[3] French Patent 801,470, May 23, 1936.

and coupled with β-naphthylamine, R-salt, and phenol.

When abietic acid was passed over the catalyst under the same conditions as used for the ester, a product was obtained which could be separated by fractional crystallization from acetone. The insoluble end was shown to be dehydroabietic acid by a comparison of its methyl ester, prepared with dimethyl sulfate, with the ester prepared from palladium-treated methyl abietate. The nitro derivatives were shown to be identical since a mixed melting point of the two showed no depression and since their analyses were the same.

The residues from the crystallization of dehydroabietic acid were fractionated under reduced pressure to remove most of the oil formed by decarboxylation. The high-boiling product was crystallized to constant melting point from methanol and esterified with dimethyl sulfate. This ester, as well as methyl dehydroabietate, showed very low unsaturation, as measured by the thiocyanate number. Also, as in the case of methyl dehydroabietate, there was no evidence of degradation, since the actual and calculated values for methoxy groups agreed very closely.

In attempts to nitrate the tetrahydro ester only decomposition products were obtained, all of which were soluble in methanol, whereas methyl dinitrodehydroabietate is extremely insoluble in this solvent. In addition to these observations, the equivalent weights of the acids as determined by careful titrations showed 299.5 for the dehydro acid having the empirical formula $C_{20}H_{28}O_2$ with the theoretical equivalent weight of 300, and 306.4 for the tetrahydro acid having the empirical formula $C_{20}H_{34}O_2$, with the theoretical equivalent weight of 306.

Experimental

Preparation of Catalyst

Asbestos Supported Catalyst (60% Pd).—One gram of acid-washed asbestos was impregnated with a solution of 1.0 g. of palladium chloride in 2 cc. of hydrochloric acid (sp. gr. 1.19) and 8 cc. of water. The mass was then mixed thoroughly with 2 cc. of 37% formaldehyde solution followed by 15 cc. of 10% sodium hydroxide (slight excess). The mass was then filtered through a conical funnel, washed twice with water, twice with 10-cc. portions of 20% acetic acid, and again with water until neutral. After drying at 95°, the catalyst was ready for use.

Alumina Supported Catalyst (4% Pd).—Fifteen grams of activated alumina (Hydralo) of 6–10 mesh was treated exactly as described for the asbestos supported catalyst. No difference in activity between the catalysts could be observed.

Disproportionation Procedure

Asbestos Supported Catalyst.—The catalyst was draped over a glass support so that it was evenly distributed throughout a large test-tube immersed in an oil-bath held at the desired temperature. The methyl abietate (α_D −45.6°) was then warmed, poured into the tube and heated for one hour at 230°. Agitation was secured by convection currents. When abietic acid (α_D −50°) was used, it was first heated to slightly above its melting point and then poured over the catalyst and treated in the same manner as methyl abietate. At the end of the reaction period, the product was poured off from the catalyst. Any catalyst suspended in the product was removed by filtration of the products through a hot funnel.

Alumina Supported Catalyst.—The catalyst was placed in an electrically heated vertical tube of 1.5–2.0 cm. diameter and the methyl abietate or abietic acid allowed to trickle over the catalyst at such a rate that the time of contact was one hour. Repeated passage of the material over the catalyst at shorter contact times to give a total contact of one hour produced the same results.

Methyl Dehydroabietate.—The crude, partly crystalline mass obtained by allowing the product of the disproportionation procedure on methyl abietate to stand was filtered with suction. The pasty mass of crystals was shaken twice with cold methanol to remove adhering oil and the residue crystallized from the same solvent. The crystals were again washed with cold methanol and dried in a vacuum desiccator over sulfuric acid. This yielded 30–45% of a product having the following properties: m. p. 60–61°; n^{99}_D 1.5081; d^{99}_4 1.0013; molecular refraction 93.4; calcd. for $C_{21}H_{30}O_2{}^{3-}$: molecular refraction, 92.7; CH_3O-, 10.02%; calcd. for $C_{21}H_{30}O_2$; CH_3O-, 9.87%; thiocyanate *no.*, 7−8;[4] calcd. *for* $C_{21}H_{30}O_2$, thiocyanate no. 0.

Methyl Dinitrodehydroabietate.—A 3-g. sample of methyl dehydroabietate was nitrated with mixed acid, the product poured into water and crystallized twice from 200 cc. of a 1:3 acetone–methanol mixture. There was obtained 1.8 g. of product melting at 192–193°. *Anal.* Calcd. for $C_{21}H_{28}N_2O_6$: N, 6.9. Found: N ($TiCl_3$ method), 6.3.

Additional crystallizations of the nitro ester gave no change in melting point nor did washing with methanol, in which the compound is quantitatively insoluble.

Methyl Diaminodehydroabietate.—Nearly theoretical yields of methyl diaminodehydroabietate were obtained by reducing the dinitro ester in methanol with hydrogen at 150° and 2000 pounds (133 atm.) pressure for two hours over a copper chromite catalyst. The catalyst was removed by filtration and, after evaporation of the solvent, the residue was crystallized from diluted methanol. The product melted at 133–134°. *Anal.* Calcd. for $C_{21}H_{32}O_2N_2$: C, 73.2; H, 9.3; N, 8.1. Found: C, 72.6; H, 9.3; N (Dumas), 7.5.

The amine hydrochloride was prepared by dissolving the free amine in dilute hydrochloric acid and concentrating to incipient crystallization. The pasty mass was diluted with 3–4 volumes of acetone, filtered, washed with acetone and dried over sulfuric acid, after which it had the

---

(4) **The thiocyanate number is a rhodanometric iodine number and on saturated compounds often gives blank values of 3–8 units.**

analysis: Calcd. for $C_{21}H_{34}N_2O_2Cl_2$: Cl, 16.76. Found: Cl, 16.92.

Dehydroabietic Acid.—The disproportionation of abietic acid was effected by the same procedure as described for methyl abietate. The product was then distilled at 2–3 mm. to free it from colored impurities. To 125 g. of distilled material there was added 170 g. of acetone and the mixture was refluxed to effect solution. After cooling, the resulting crystals were washed with cold acetone and air dried. Successive concentrations of the mother liquor from the first and succeeding crystallizations gave additional material.

The combined yield of dehydroabietic acid was 72 g. This acid had the following properties: m. p. 166–167°, n^{22}D 1.5370, αD +60.5°, neut. equiv., 299.5. Upon methylation of this acid with dimethyl sulfate and nitration of the ester, there was obtained a 35–40% yield of nitro derivative melting at 192–193° and showing no depression when mixed with methyl dinitrodehydroabietate.

Tetrahydroabietic Acid.—The combined residues from several dehydroabietic acid crystallizations were worked up as follows. The viscous liquid containing some acetone was heated to 200° to remove solvent and then vacuum distilled according to the scheme.

Fraction	B. p., °C., at 6–7 mm.	A. N.
1	Up to 210	33
2	210–232	99
3	232–240	164
4	240–Dry	168

Fractions 3 and 4 were combined and recrystallized twice from methanol, after which the product had the following constants: m. p. 159°; n^{22}D 1.5408; neut. equiv., 306.4.

Upon conversion to the methyl ester by the methods previously described and vacuum distillation, a product was obtained which had the following properties: b. p. 185–190° at 5–7 mm.; CH_3O, 9.6%; calculated for $C_{21}H_{36}O_2$, CH_3O, 9.7%; A. N., 4.0; thiocyanate no., 5; n^{20}D 1.5306; d^{20}_4 1.0506; mol. refraction 94.9; calculated for $C_{21}H_{36}O_2$, mol. refraction 94.2.

Summary

A simplified method for the preparation of dehydroabietic acid and methyl dehydroabietate is presented. The preparation and properties of methyl diaminodehydroabietate are described. Additional evidence on the disproportionation of abietic acid over a palladium catalyst has been secured.

WILMINGTON, DELAWARE RECEIVED MARCH 28, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 168]

The Condensation of Aliphatic Alcohols with Aromatic Hydrocarbons. I. The Preparation of Mesitylene and *sym*-Triethylbenzene

BY JAMES F. NORRIS AND JOHN N. INGRAHAM

The recent publication of a paper[1] describing the condensation of primary aliphatic alcohols with benzene by means of aluminum chloride, makes it desirable to describe, at this time, a part of the results obtained in this Laboratory in an investigation of such reactions. For several years the condensations of aliphatic alcohols, ethers, and esters of organic acids have been studied systematically and noteworthy results have been obtained. Alkylation of aromatic hydrocarbons has been accomplished with the three classes with satisfactory yields. In the case of esters, it was found possible to introduce into aromatic hydrocarbons both alkyl and acyl groups.

Tzukervanik and Vikhrova in their paper state that they were unable to get any satisfactory results with methyl alcohol and benzene. The methylation products obtained from toluene they considered to be produced by the action of aluminum chloride on the hydrocarbon. With ethyl alcohol and benzene, ethylbenzene and a number of more highly substituted derivatives were obtained; the isomers were not separated and the quantities of the several fractions are not stated.

In our experiments with methyl and ethyl alcohols we studied particularly the conditions necessary to produce the largest yields of the pure symmetrical trialkylated hydrocarbons. In the study of the mechanism of the condensation, which will be reported in detail later, it was shown that the two alcohols react with aluminum chloride and form compounds having the formula $ROAlCl_2$, which decompose when heated and produce RCl + AlOCl. In the presence of additional aluminum chloride, the usual Friedel–Crafts synthesis takes place. It has been shown in this Laboratory that in the condensation of alkyl halides with benzene the polyalkylated hydrocarbons formed are determined largely by the molecular ratio of the benzene and alumi-

---

[1] Tzukervanik and Vikhrova, *J. Gen. Chem. U. S. S. R.*, **7**, 632 (1937); *C. A.*, **30**, 5779^5 (1937).