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, α_D +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-

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

num chloride used. With the ratio of less than 1 of chloride to 1 of benzene a great variety of derivatives was formed. When the ratio was 2 of aluminum chloride, $AlCl_3$, to 1 of benzene and 3 of the halide the chief product was the symmetrical trialkylated derivative. These facts were taken into account in the condensation of the alcohols with benzene and toluene. The methods give good yields of the desired hydrocarbons, which can be obtained readily for further investigation.

Experimental

Preparation of Mesitylene.—To 355 g. (8/3 mole) of a good grade of commercial aluminum chloride in a 1-liter three-necked flask fitted with a dropping funnel, a mechanical stirrer, and an adapter carrying a condenser and thermometer, all the openings being protected by calcium chloride tubes, 30.7 g. (1/3 mole) of toluene is added, the mixture cooled in an ice-bath to 10–15°, and a mixture of 30.7 g. (1/3 mole) of toluene and 42.7 g. (4/3 mole) of methanol added dropwise during one-half hour. The ice-bath is then replaced by an oil-bath previously heated to 110°, the dropping funnel removed and dry air passed through the reaction mixture at the rate of 2–3 bubbles per second during the heating period. After the mixture has reached a temperature of 108–110°, it is maintained within this range for three hours, allowed to cool and decomposed by pouring into a 3-liter flask containing 1 liter of chipped ice and 50 cc. of concentrated hydrochloric acid. The reaction flask is rinsed with cold water and the washings added to the decomposition mixture. This is distilled with steam and the hydrocarbon separated and dried.

The crude product is sulfonated by digestion for one hour with concentrated sulfuric acid (1.65 cc. per g.) on a steam-bath in a flask provided with a reflux condenser. After cooling somewhat, concentrated hydrochloric acid (2.72 cc. per cc. of sulfuric acid used) is added through the condenser, the first portions being introduced very cautiously, after which the heating is continued for two hours. The product is then poured into 1 liter of cold water in a 3-liter flask and the mixture distilled with steam. The mesitylene is separated, dried and distilled through a 65-cm. V-packed column having 17 theoretical plates; b. p. 164–165°; yield 56–60 g. This material (92 cc.) redistilled through the same column gave a fore-fraction of 2 cc., b. p. 162.6–164.3°, and a main fraction of 83 cc., b. p. 164.3–164.6°. A sample of mesitylene, b. p. 164–165°, made by condensing methyl bromide with benzene, as will be described later, was shown by a cooling curve to be over 99% pure.

m-Xylene also has been used as a starting material (*m*-xylene 1, methanol 1, aluminum chloride 3 mol), giving somewhat higher yields of mesitylene of the same boiling range.

sym-Triethylbenzene.—Thirty-two and eight-tenths grams of benzene, 42.6 g. of ethanol, and 206 g. of aluminum chloride are mixed in the same way as for mesitylene and heated for three hours on a steam-bath. After decomposition and steam distillation, the sulfonation is carried out with the same proportions of reactants and under the same conditions as for mesitylene. For hydrolysis, 2 cc. of concentrated hydrochloric acid per cubic centimeter of sulfuric acid used is employed. The mixture is heated for two hours on the steam-bath, diluted and steam distilled. The hydrocarbon layer is triethylbenzene, b. p. 214–215°, weight 35–38 g.

One hundred and thirty cubic centimeters of the hydrocarbon (the combined product of several runs) was distilled slowly through a 26-inch (66 cm.), V-packed Fenske column having 17 theoretical plates. Refractive indices were taken of drops of distillate from time to time. It was found that with the exception of the first 3 cc., and the final 10 cc., these indices were constant at 1.4956 (taken at 18.1° with Abbe refractometer). The holdup of the column is 3 cc. There was thus obtained 112 cc. of hydrocarbon having a constant refractive index; b. p. 214.8° at 755.1 mm. (corr.).

This hydrocarbon was steam distilled, and refractive indices again taken. The hydrocarbon came over without change in the refractive index.

The material having a constant refractive index during both distillations (108 cc.) was considered to be pure.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.31, 88.69; H, 11.29, 11.34.

A mixture of 6 cc. of hydrocarbon, 44 g. of chromic anhydride, and 500 cc. of 25% sulfuric acid was boiled gently for twenty-four hours under a return condenser. The condenser was then changed for distillation and a few cubic centimeters distilled. About 0.5 cc. of hydrocarbon was thus obtained. The mixture was cooled and filtered, and the filtrate extracted several times with ether. After the evaporation of the ether, a yellow solid was obtained which was added to that on the filter. About 4 g. of slightly yellow product resulted, m. p. (crude) 376–378°.

The crude product was dissolved in 5% sodium hydroxide, the solution filtered and strongly acidified with concentrated hydrochloric acid. The acid was filtered off, and the filtrate extracted as before. The product was recrystallized from boiling water. It had the appearance of salt crystals, and melted at 379° (corr.). It was trimesic acid, therefore, and its isolation demonstrated that the hydrocarbon obtained from the condensation of ethyl alcohol and benzene under the conditions specified is symmetrical triethylbenzene.

Four cc. of hydrocarbon and 20 cc. of bromine were placed in a 50-cc. flask covered with tin foil and cooled in an ice-bath. A crystal of iodine was added, and a reflux condenser attached by means of a ground glass joint. When the material had cooled, the bromine was added slowly. The mixture was allowed to stand overnight. It was then poured into cold 10% sodium hydroxide and stirred until it formed solid lumps. The sodium hydroxide was decanted through a filter, and a fresh portion added. The mixture was boiled, cooled and filtered: crude yield 8.7 g.; m. p. 103–104°. The product was recrystallized from absolute alcohol and dried in a vacuum oven at 50°: yield 8 g.; m. p. 104.6–104.8°. This melting point was not changed by subsequent recrystallizations. The recorded melting points vary from 103 to 106°.

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(2) Melting and boiling points were taken with a short range calibrated thermometer. For boiling points this was used at total immersion; for melting points the length of exposed steam was 1.3 cm. at 104° and 2.3 cm. at 112°. Melting points were taken in a copper block.

Anal. Calcd. for $C_{12}H_{15}Br_3$: Br, 60.09. Found: Br, 59.70, 59.74.

Sixteen cc. of concentrated sulfuric acid and 19 cc. of fuming nitric acid (d. 1.50) were mixed and placed in a 50-cc. flask attached to a reflux condenser with a ground glass joint. The mixed acids were cooled in an ice-bath and 4 cc. of hydrocarbon added slowly. The reaction was completed by refluxing gently for fifteen minutes. After cooling, the mixture was poured into cold water and the precipitated nitro-compound filtered off. It was washed and dried: crude yield 6 g.; m. p. 111.5–112°. The product was recrystallized from absolute alcohol, then from a dioxane–water mixture, and finally from absolute alcohol; m. p. 112.4–112.6°. The recorded melting point is 108–109°.

Anal. Calcd. for $C_{12}H_{15}N_3O_6$: N_2, 14.16. Found: N_2, 14.15, 14.24.

Summary

Methods are described for the preparation of mesitylene by condensing methyl alcohol with toluene or *m*-xylene in the presence of aluminum chloride and for the preparation of symmetrical triethylbenzene from ethyl alcohol and benzene.

CAMBRIDGE, MASS. RECEIVED MARCH 22, 1938

[CONTRIBUTION FROM THE LABORATORIES OF ARTHUR D. LITTLE, INC.]

A New Substance, Cativic Acid, and its Preparation, Properties and Derivatives

BY NICHOLAS L. KALMAN

The "Cativa" tree, *Prioria copaifera*, Griseb.,[1] is found extensively in the lowlands bordering the Caribbean Sea from Mexico into Colombia, the trees reaching a diameter up to 5 ft. (1.5 meters) and a height of 100 ft. (30 meters). It yields a copious oleo-resinous exudate about which very little has been learned until recently. Fawcett[2] reported that this substance, resembling copaiba balsam, was soluble in many organic solvents, insoluble in water, reacted with aqueous and fused alkalies and gave 90% of a wide-boiling product on destructive distillation. Dirmitt,[3] after noting the involatility of the exudate, found hydrocarbons in the cracked distillate, and, by analysis, the formula $C_{24}H_{40}O_2$. Umney[4] reported some properties and that the exudate (now called "Cativo") was chiefly an acid resin. Weigel[5] pronounced the substance to be a "resinol-acid resin," observed the same characteristics as Umney and reported 75–80% resin acids, 13% unsaponifiable, 2% essential oil and 3% water and foreign matter.

Experimental

Preliminary Examination.—Investigation of Cativo samples from different places and taken at different times of year indicated a fairly uniform composition, the exudate being very sticky, viscous, with a cold flow and a muddy brown color due to fine suspended matter. When this is removed and the 0.5% of water evaporated, the product is clear and transparent. The cativo is insoluble in water, contains less than 2% of volatile oil and no free or esterified benzoic or salicylic acid. Over 95% appears to consist of a high boiling cyclic acid and its ester with the corresponding alcohol, which classifies cativo as a resin. Previous observations[4,5] were confirmed: (averages) acid no., 149.5; sap. no., 169.2; ester no., 19.7. There was also found 0.4% of an acid extractable from the ethereal solution with sodium bicarbonate; acid no., 373.6.

Separation of Cativic Acid.—A filtered solution of cativo in petroleum ether was first shaken out with sodium bicarbonate, then carefully neutralized with 0.5 *N* alcoholic potassium hydroxide, and diluted with water until the alcohol content was 50%. The aqueous–alcoholic layer was then separated, and washed several times with petroleum ether. An excess of hydrochloric acid precipitated the acid, which was dissolved in petroleum ether, dried with calcium chloride, the solvent distilled and the residue dried at 100° at a 1-mm. pressure, to a brown, viscous, tacky semi-solid. To this acid we have given the name "Cativic acid."

Vacuum distillation results in decomposition of the cativic acid, unless the pressure is reduced to 5 mm. or less. At 1 mm. it comes over as an odorless, water-white, viscous liquid at 194–195°. Crystallization could not be induced, even by fractional vacuum distillation (20 fractions), decomposition of the purified salts or from aqueous alcohol or acetone.

Anal. Calcd. for $C_{20}H_{34}O_2$: C, 78.36; H, 11.19; acid no., 183.2; mol. wt., 306. Found: C, 78.41; H, 11.06; acid no., 182.2; mol. wt. (f. p. of camphor), 296. Calcd. for $Al(C_{20}H_{33}O_2)_3$: Al, 2.98. Found: Al, 2.86.

The Ester, Cativyl Cativate.—The residual acid-free petroleum ether solution of cativo is washed several times with 50% aqueous alcohol, dried with calcium chloride, and the petroleum ether distilled off. Vacuum distillation of the residue in a nitrogen atmosphere at about 5 mm. removes a volatile oil below 100°, but the pleasant smelling, mobile residue will not distil even at 250°. Hydroly-

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[1] Griesebach, "Flora of the British West Indies."

[2] Wm. Fawcett, *Bull. Bot. Dept., Jamaica*, N. S., **4**, 77–78 (1897).

[3] Charles W. Dirmitt, "Contribution from the Chemical Laboratory of the Philadelphia College of Pharmacy, No. 172," *Am. J. Pharm.*, **70**, 10–18 (1898).

[4] E. M. Holmes, *Pharm. J.*, [4] **15**, 296 (1902).

[5] G. Weigel, *Pharm. Zentralhalle*, **44**, 147–150 (1903).