A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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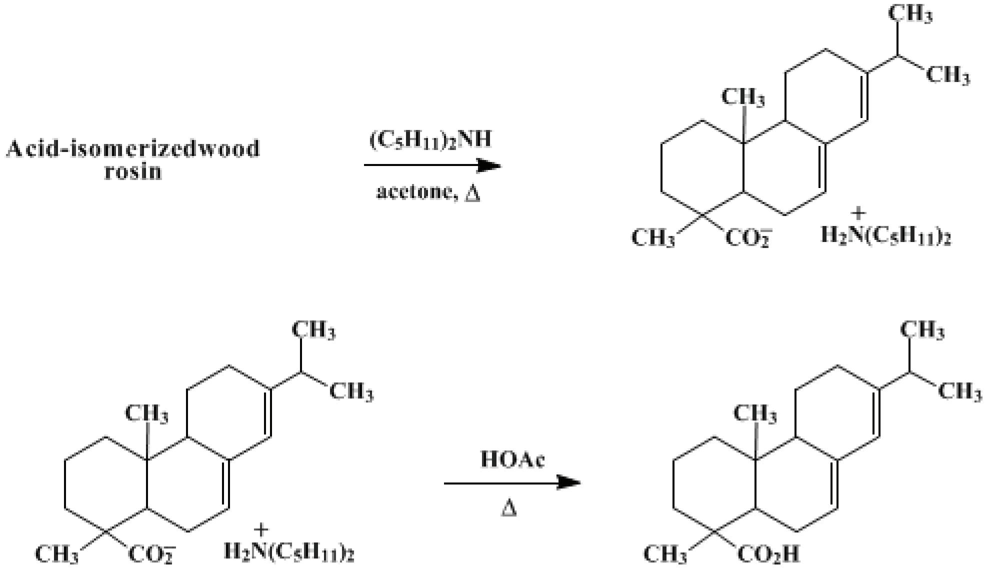
ABIETIC ACID



Submitted by G. C. Harris and T. F. Sanderson[1].
Checked by R. T. Arnold and K. L. Lindsay.

1. Procedure

In a 2-l. round-bottomed flask fitted with a 35-cm. reflux condenser are placed 250 g. (0.74 mole) of N-grade wood rosin (Note 1), 740 ml. of 95% ethanol, and 42 ml. of hydrochloric acid (sp. gr. 1.19). A stream of carbon dioxide is passed over the surface of the solution by means of a glass tube which extends downward through the condenser during this reaction (Note 2). The mixture is boiled under reflux for 2 hours (Note 3). At the end of this time, the ethanol and acid are removed by steam distillation and the water is decanted. The residue is cooled to room temperature and dissolved in 1 l. of ether. The ether solution is extracted with water and dried over 200 g. of anhydrous sodium sulfate. The bulk of the ether is evaporated on the steam bath, and the last traces are removed by fusing the rosin over a free flame and under a vacuum furnished by a water aspirator. The molten rosin, blanketed continuously with carbon dioxide, is most conveniently handled by being poured into a paper boat; yield 245 g.; $[\alpha]_D^{24}$ −35° (Note 4).

The isomerized rosin, 245 g. (0.72 mole) (Note 1), is placed in a 1-l. Erlenmeyer flask and dissolved in 375 ml. of acetone by heating the mixture on a steam bath. To this solution, at incipient boiling, is added slowly and with vigorous agitation (Note 5) 127 g. (0.81 mole) of diamylamine[2] (Note 6). Upon cooling to room temperature, crystals appear in the form of rosettes. The mass is agitated, cooled well in an ice bath, and filtered by suction. The crystalline salt is washed on a Büchner funnel with 150 ml. of acetone and dried in a vacuum oven at 50° for 1 hour. The optical rotation of this material is $[\alpha]_D^{24}$ −18° (Note 4). The solid is recrystallized four times from acetone. Each time a sufficient quantity (20 ml. per g.) of acetone is used to obtain complete solution, and the solvent is evaporated until incipient precipitation of the salt occurs. The yield of product is 118 g.; $[\alpha]_D^{24}$ −60° (Note 4). An additional 29 g. of product, having the same rotation, can be recovered from filtrates of the previous crystallizations.

The amine salt (147 g.) is placed in a 4-l. Erlenmeyer flask and dissolved in 1 l. of 95% ethanol by heating the mixture on a steam bath. To the solution, which has been cooled to room temperature (Note 7), is added 39 g. (35.8 ml.) of glacial acetic acid, and the solution is stirred. Water (900 ml.) is added cautiously at first and with vigorous agitation until crystals of abietic acid begin to appear; the remainder of the water is then added more rapidly. The abietic acid is collected on a Büchner funnel (Note 8) and washed with water until the acetic acid has been removed completely as indicated by tests with indicator paper. Recrystallization can be effected by dissolving the crude product in 700 ml. of 95% ethanol, adding 600 ml. of water as described above, and cooling the solution. The yield of abietic acid is 98 g. (40% based on the weight of isomerized rosin; $[\alpha]_D^{24}$ −106° (Note 4) and (Note 9). The ultraviolet absorption spectrum shows a maximum at 241 mμ; α = 77.0 (Note 10).

2. Notes

1. The calculation of molar quantities is based on an acid number of 166 for N-grade wood rosin as obtained from Hercules Powder Company, Wilmington, Delaware. Acid number is the number of milligrams of potassium hydroxide required to neutralize 1 g. of sample.
2. Blanketing the rosin in solution or in the molten state with carbon dioxide serves to keep it out of contact with air to avoid oxidation.
3. The maximum negative optical rotation, $[\alpha]_D^{24}$ −35°, is obtained with a minimum reflux time of 2 hours.
4. Rotations are reported as those of 1% solutions in absolute ethanol.
5. The addition of the amine to the hot solution is necessary for the formation of the salt. However, it must be done slowly and with rapid stirring because of the resulting vigorous exothermic reaction.
6. Commercial diamylamine, a mixture of isomers, purchased from Sharples Chemicals Company, Philadelphia, Pennsylvania, was employed.
7. The acid is added to a cooled solution of the salt in ethanol to minimize the chance for isomerization of the liberated abietic acid.
8. An early filtration is desirable for the purpose of removing the abietic acid from the acidic solution where isomerization can take place. Washing with a large volume of water and recrystallizing assures the complete removal of acetic acid.
9. The pure acid is dried in a vacuum desiccator over sodium hydroxide or calcium sulfate and stored in an oxygen-free atmosphere. Undue exposure to higher temperatures will result in isomerization, and contact with oxygen will result in oxidation.
10. The absorption spectrum data were obtained from measurements made with a Beckman Ultraviolet Spectrophotometer. The formulas employed in making the calculations use the term α, specific absorption coefficient. $\alpha = \log_{10} I_0/I/cl$ where I_0 = intensity of radiation transmitted by the solvent; I = intensity of radiation transmitted by the solution; c = concentration of solute in grams per liter; l = length in centimeters of solution through which the radiation passes.

3. Discussion

Abietic acid has usually been prepared[2] from rosin through the acid sodium salt ($3C_{20}H_{30}O_2 \cdot C_{19}H_{29}CO_2Na$) with the subsequent formation and recrystallization of the diamylamine salt. The acid is regenerated from the pure salt by decomposition of the latter with a weak acid such as acetic acid. In addition, it has been purified[3] through the potassium, piperidine, and brucine salts, as well as through abietic anhydride and trityl abietate. The acid is regenerated from the pure salts by decomposition of the latter with a weak acid such as acetic acid, and from the pure acid derivatives by treatment with potassium hydroxide.

Two improvements have been introduced in the first method[2] by the procedure described above: (1) the abietic content of the rosin is increased by isomerization, and (2) a much better recovery of acid is obtained by applying the amine salt technique directly to the isomerized rosin, thus eliminating the step involving the acid sodium salt.

References and Notes

1. Hercules Powder Company, Wilmington, Delaware.
2. Palkin and Harris, *J. Am. Chem. Soc.*, **56**, 1935 (1934).
3. Lombard and Frey, *Bull. soc. chim. France*, **1948**, 1194.

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

sodium sulfate (7757-82-6)

oxygen (7782-44-7)

carbon dioxide (124-38-9)

calcium sulfate (7778-18-9)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

piperidine (110-89-4)

potassium (7440-09-7)

brucine

ABIETIC ACID (514-10-3)

diamylamine (2050-92-2)

abietic anhydride

trityl abietate