

Anal. calcd. for $C_3H_7Cl_2OP$: C, 22.38; H, 4.38; Cl, 44.05; P, 19.24. Found: C, 22.36; H, 4.43; Cl, 44.24; P, 19.32.

Tetrakis(bromomethyl)phosphonium Bromide (VI). Bromine (131.0 grams, 0.818 mole) was added dropwise with vigorous stirring to a flask containing 30.0 grams (0.157 mole) of tetrakis(hydroxymethyl)phosphonium chloride and 221.8 grams (0.818 mole) of phosphorus tribromide in 500 ml. of carbon tetrachloride. The bromine was added at a rate such that the temperature did not exceed $50^\circ C$. The mixture, which contained a large amount of solid, was then refluxed for 6 hours. During this time the mixture turned from a dark red color to a yellow color. The cooled mixture was filtered, and yielded 71.3 grams (93% yield) of crude VI. Pure white crystals, m.p. $242-3^\circ C$., were obtained after two recrystallizations from benzene-methanol. The infrared spectrum (KBr) exhibited peaks at 3.28 (m), 3.35 (m), 7.05 (w), 7.2 (m), 8.23 (w), 8.43 (w), 8.78 (w), 8.95 (w), 9.08 (w), 9.2 (w), 11.7 (s), 11.95 (s), and 12.35μ (w).

Anal. calcd. for $C_4H_8Br_5P$: C, 9.86; H, 1.64; Br, 82.13; P, 6.40. Found: C, 10.00; H, 1.80; Br, 81.98; P, 6.37.

Tris(bromomethyl)phosphine Oxide (V). VI (71.3 grams, 0.148 mole) was placed in 200 ml. of water, and solid sodium bicarbonate was added with stirring until the solution was alkaline. The oil layer, consisting of crude tris(bromomethyl)phosphine, was separated from the water layer. It had a disagreeable odor resembling that of tris(chloromethyl)phosphine. Tetrahydrofuran was added to the oil and an excess of 3% aqueous hydrogen peroxide was gradually added with stirring. The reaction temperature was not allowed to go above $50^\circ C$. After stirring for 2 hours at room temperature, the solution was evaporated to a solid mass. The solid was triturated with hot chloroform. After the chloroform evaporated, 36.8 grams (71% yield) of crude V was obtained. Pure white crystals, m.p. $126.5-127.5^\circ C$., were obtained after three recrystallizations from cyclohexane. The infrared spectrum (KBr) exhibited peaks at 3.28 (w), 3.35 (w), 7.2 (w), 8.2 (s) with a shoulder at 8.3 (w), 8.58 (w), 9.15 (w), 9.32 (w), and 12.25 (s) with a shoulder at 12.15μ (s).

The NMR spectrum of a deuteriochloroform solution of V showed a doublet centered at δ 3.88 p.p.m., Jp-ch = 7 c.p.s.

Anal. calcd. for $C_3H_6Br_3OP$: C, 10.94; H, 1.82; Br, 72.95; P, 9.42. Found: C, 10.97; H, 1.85; Br, 72.72; P, 9.64.

Methyl Bis(iodomethyl)phosphine Oxide (VII). IV (10.0 grams, 0.062 mole) and 20.0 grams (0.133 mole) of sodium iodide were refluxed in 300 ml. of acetone for 35 hours. The hot solution was filtered to remove the sodium chloride. When the filtrate had cooled, 9.9 grams (46.7% yield) of crude VII were obtained. Pure white crystals m.p. $176-77^\circ C$., were obtained by recrystallization from 50% aqueous dimethylformamide. The infrared spectrum (KBr) exhibited peaks 3.3 (w), 3.38 (w), 7.2 (w), 7.3 (w), 7.63 (m), 8.32 (s) with a shoulder at 8.55 (w), 8.75 (w), 8.9 (w), 9.4 (w), 9.53 (w), 11.0 (s), 11.3 (w), 12.3 (m), and 13.1μ (m).

The NMR spectrum of deuteriochloroform solution of VII showed a doublet centered at δ 1.92 p.p.m., Jp-ch = 13 c.p.s. and a doublet centered at δ 3.41 p.p.m., Jp-ch = 7 c.p.s. in a ratio of 3 to 4, respectively.

Anal. calcd. for $C_3H_7I_2OP$: C, 10.47; H, 2.04; I, 73.82; P, 9.02. Found: C, 10.57; H, 2.09; I, 73.62; P, 9.08.

ACKNOWLEDGMENT

The authors thank Sylvia H. Miles for the infrared analyses and Gordon J. Boudreaux for the NMR analyses.

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RECEIVED for review September 14, 1966. Accepted November 30, 1966. The Southern Regional Research Laboratories is one of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Mention of trade names does not imply their endorsement by the USDA over instruments not mentioned.

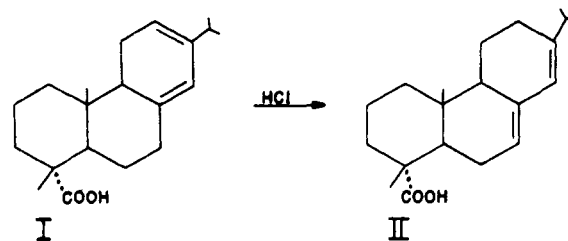
Levopimaric Acid as a Ready Source of Abietic Acid

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A simple process for the preparation of abietic acid from levopimaric acid is described.

ABIETIC ACID (II), a major resin acid of pine gum and of most all types of rosin, is generally prepared for laboratory use by isolation from rosin (2). This procedure is relatively laborious. Furthermore, abietic acid is not stable on storage. Small amounts are generally freshly prepared immediately before use.

The availability of pure levopimaric acid (I) from pine gum (3, 4) has led the authors to develop a very simple process for its conversion to abietic acid. Levopimaric acid is a stable compound and can be stored for years without decomposition. Thus it provides an ideal source for a ready supply of freshly prepared, pure abietic acid. The procedure



involves the acid isomerization of the homocyclic diene to the heterocyclic diene in the presence of acid.

PROCEDURE

Levopimaric acid of $[\alpha]_D^{25} -276^\circ$ (*c* 2 in 95% ethanol; 59.4 grams; 0.196 mole) was dissolved in 1 liter of 0.12*N* ethanolic hydrochloric acid prepared by diluting 10.0 ml. of concentrated hydrochloric acid to 1.0 liter with absolute ethanol (1). The specific rotation was constant at $[\alpha]_D^{25} -90.5^\circ$ after 21 hours at room temperature. (The rotation using 95% ethanol was -85.0° .) Two hundred milliliters of water was added slowly with stirring. The abietic acid which crystallized out weighed 31.6 grams (53%); $[\alpha]_D^{25} -102^\circ$ (*c* 2 in 95% ethanol); $\lambda_{\max}^{\text{EtOH}}$ 241 *m* μ , α 74.5, and is generally considered pure enough for most uses—literature (2) cites $[\alpha]_D^{25} -106^\circ$ for pure abietic acid. After one recrystallization from aqueous ethanol the product exhibited $[\alpha]_D^{25} -106^\circ$ (*c* 2.0 in 95% ethanol). [An additional 600 ml. of water was added to the original filtrate and 23.8 grams (40%) of abietic acid of $[\alpha]_D^{25} -94.6^\circ$ (*c* 2 in 95% ethanol) was obtained.] Abietic acid is best stored under nitrogen in the freezing compartment of a refrigerator.

ACKNOWLEDGMENT

This research was conducted while author Hiroshi Takeda was pursuing a postdoctoral resident research associateship under the auspices of the National Academy of Sciences-National Research Council.

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RECEIVED for review October 21, 1966. Accepted December 16, 1966. The Naval Stores Laboratory is one of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

CORRECTION

In the article "Enthalpies, Entropies, and Free Energy Functions of TlF, TlBr, and TlI Above Room Temperature" by Daniel Cubicciotti and Harold Eding [*J. CHEM. ENG. DATA* 10, 343 (1965)], the following corrections should be made:

Westrum (1) has recently measured the low temperature heat capacity of TlF and derived an absolute entropy S_{298}° (TlF, C) = 22.87 e.u. This value is 3 e.u. smaller than the value we derived from vaporization data. Therefore, the free energy functions we quoted in Table II of the original paper should be revised to the following:

| $T, ^\circ\text{K.}$ | $-(F^\circ - H_{298}^\circ)/T$ E.U. |
|----------------------|--|
| 298 | 22.87 |
| 355 | 23.06 |
| 355 | 23.06 |
| 400 | 23.40 |
| 500 | 24.41 |
| 595.4(c) | 25.48 |
| 595.4(l) | 25.48 |
| 700 | 27.57 |
| 800 | 29.32 |
| 900 | 30.93 |
| 1000 | 32.39 |
| 1250 | 35.55 |

- (1) E.F. Westrum, Jr., private communication.

CORRECTION

In the article "Solid-Liquid Equilibrium in the Benzene-Pyridine System" by F.J. Cioffi and C.E. Messer [*J. CHEM. ENG. DATA* 11, 532 (1966)], Figures 1 and 4 were reversed.
