

On the Conversion of *l*-Abietic Acid into a *d*-Abietic Acid

BY TORSTEN HASSELSTROM AND JOHN D. MCPHERSON

The addition of hydrogen chloride to abietic acid produces dichlorodihydroabietic acid which is crystalline and easily purified.¹ We have found that dichlorodihydroabietic acid may be obtained directly from rosin and in apparently equal purity as when Steele's abietic acid² is used as a starting material. On splitting off of hydrogen chloride from dichlorodihydroabietic acid with sodium ethoxide, we have been able to obtain an abietic acid with the positive sign of rotation. This seemingly new abietic acid was characterized through its di-*n*-amylamine salt. According to Levy,¹ the dichlorodihydroabietic acid produces an abietic acid with the negative sign of rotation when heated at its melting point, and when treated with quinoline.

Experimental

Dichlorodihydroabietic Acid.—This compound was prepared substantially according to the directions given by Levy.¹ Ninety-five grams of "X" grade gum rosin was dissolved in 70 cc. of glacial acetic acid and boiled for four hours. The solution was then cooled to about 0°. The semi-solid mixture was saturated with dry hydrogen chloride, the bottle sealed and the mixture left standing at room temperature for two weeks. It was then filtered and the solid collected; yield 26 g. It was recrystallized from acetone and then from ethyl acetate, m. p. 190.5° dec. (corr.); (α)_D -10° (in ethanol).

Anal. Calcd. for C₂₀H₃₂O₂Cl₂: C, 63.97; H, 8.59. Found: C, 63.76; H, 8.60.

The dichlorodihydroabietic acid prepared from Steele's abietic acid,² m. p. 163.5–165° (corr.); (α)_D -76° (in ethanol) showed the following constants: m. p. 190.5° dec. (corr.); (α)_D -8.1 (in ethanol). Found: C, 63.96; H, 9.16.

***d*-Abietic Acid.**—Ten grams of dichlorodihydroabietic acid (m. p. 190.5° dec. (corr.); (α)_D -10°), was added in portions over a period of five to ten minutes to a boiling solution of sodium ethoxide (17.5 g. of sodium and 175 cc. of absolute ethanol). The mixture was refluxed for one hour. Water was then added and the excess of alcohol was distilled off. As much of the liquid as possible was poured off the remaining solid. The soapy residue was then dissolved in 3 liters of water. The solution was filtered and the filtrate acidified with dilute hydrochloric acid. The white precipitate was filtered off and crystallized from methanol, yield 3.5 g. (40%), m. p. 137–139°; (α)_D +27° (in ethanol), which on successive crystallization yielded an abietic acid melting at 142–143° (corr.); (α)_D +20° (in ethanol). Calcd. for C₂₀H₃₀O₂: C, 79.40; H, 10.05. Found: C, 79.33; H, 10.08; C, 79.57; H, 10.32.

(1) Røy and Simonsen, *Indian Forest Records*, **11**, 211 (1924); Levy, *Ber.*, **64**, 2441 (1931).

(2) Steele, *This Journal*, **44**, 1333 (1922).

The mother liquor from this separation yielded small quantities of an acid melting at 207–212° (corr.), probably identical with the dihydroabietic acid of melting point 217.5–218.5° (corr.), previously described by us.³

A solution of 6 g. of *d*-abietic acid of m. p. 139–143° (corr.) was treated with 4 g. of di-*n*-amylamine (Eastman Kodak Company) in acetone. The solution was boiled for about ten minutes and filtered. On standing 10.6 g. of crude di-*n*-amylamine salt was obtained, m. p. 117.5–119° (corr.). The compound was recrystallized four times, the melting point remaining constant after the third crystallization, being 119–119.5° (corr.), (α)_D +3.3° (in ethanol). The amounts of recovered di-*n*-amylamine salt were too small to be converted into the original acid.

Anal. Calcd. for C₃₀H₅₀O₂N: C, 78.35; H, 11.62. Found: C, 78.61; H, 11.76.

The di-*n*-amylamine salt of *l*-abietic acid shows the following constants: m. p. 141–142°; (α)_D -74.5°.⁴

This investigation is being continued.

(3) Hasselstrom and McPherson, *ibid.*, **61**, 1228 (1939).

(4) Palkin and Harris, *ibid.*, **56**, 1935 (1934).

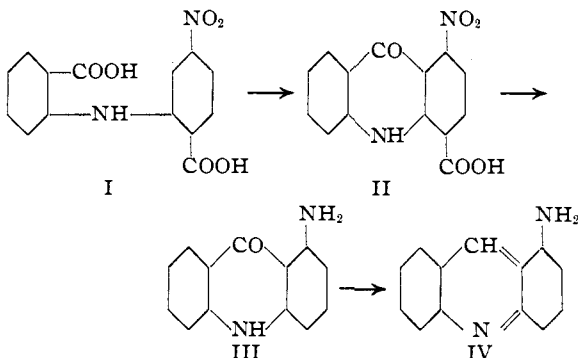
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The Identification of 1-Nitroacridone-4-carboxylic Acid as 1-Aminoacridine

BY KONOMU MATSUMURA

In a previous paper,¹ it was stated that the nitroacridone-carboxylic acid (m. p. 333° dec.) which was obtained from 5-nitrodiphenylamine-2,2'-dicarboxylic acid (I) by ring closure should have the constitution of 1-nitroacridone-4-carboxylic acid (II) in consideration of the observations that the fluorescence and solubility of the aminoacridone (III), which was converted from the nitroacridonecarboxylic acid in question, exactly coincided with those of 1-aminoacridone but were widely different from those of the 3-isomer.



The present paper indicates the previous interpretation to be altogether correct, but not in harmony with the Lehmstedt conclusion,² on

(1) Matsumura, *This Journal*, **60**, 591 (1938).

(2) Lehmstedt and Schlader, *Ber.*, **70**, 1526 (1937); Lehmstedt, *ibid.*, **71**, 1609 (1938).

TABLE I
COMPARISON OF THE PROPERTIES OF SUBSTITUTED ACRIDINES

Substituent	1-Amino-	3-Amino-
Fluorescence in alc. soln.	None	Intense green
M. p., °C.	{ 178 (uncorr.) 182.3 (corr.) ^a	{ 218 (uncorr.) ^b 223.5 (corr.)
Hydrochloride {	Cryst. color	Blue-black
	Aq. soln.	Violet-red color with no fluores.
	M. p., °C. (uncorr.)	285 (dec.) ^c
		Orange-red
		Orange-yellow color with green fluores.
		328-329 (dec.)

^a Albert and Linnell [*J. Chem. Soc.*, 22 (1938)] give m. p. 181° (corr.), and Lehmkstedt [*Ber.*, 71, 808 (1938)] gives m. p. 165-170°. ^b Albert and Linnell [*J. Chem. Soc.*, 1618 (1936)] give m. p. 219° (corr.) and Scherlin [*Ann.*, 516, 218 (1935)] m. p. 221-222° for their products, respectively. ^c Lehmkstedt (*loc. cit.*) gives m. p. 286° (dec.) for his product.

the basis of further investigations as follows. The aminoacridine (IV) which was obtained from the aminoacridone in question (III), on admixture with synthesized 3-aminoacridine, showed a great depression of the melting point, while with synthetic 1-aminoacridine it showed no depression; moreover, its other properties were in good agreement with those of 1-aminoacridine shown in Table I.

The nitroacridone-carboxylic acid must, therefore, be 1-nitroacridone-4-carboxylic acid.

Experimental

1-Aminoacridine.—Four-tenths gram of the aminoacridone in question (m. p. 289-290°) and 5 g. of sodium amalgam (5%) in 30 cc. of dilute alcohol (33%) were heated on a water-bath for three hours with frequent shaking. The solution was decanted from mercury, acidified with hydrochloric acid and oxidized with 2 g. of ferric chloride. The base (yield, 0.25 g.) which was set free from the hydrochloride, crystallized from alcohol (33%) into gold-yellow prismatic needles, melting at 178° alone or on admixture with a sample of 1-aminoacridine (m. p. 178°), whereas a mixture (7:3) of this compound with an authentic specimen of 3-aminoacridine (m. p. 218°) melted at 135-140°.

Anal. Calcd. for C₁₃H₁₀N₂: C, 80.41; H, 5.15. Found: C, 80.22; H, 5.28.

The hydrochloride gives blue-black prismatic needles from dilute hydrochloric acid (5%), m. p. 285° (dec.). The aqueous solution assumes a violet-red color, while an alcoholic solution has a violet-blue color, both showing no fluorescence in any dilution.

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Synthesis of Aldehydes by Stephen's Method¹

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The application of Stephen's² procedure to the preparation of several aldehydes has led to the conclusion that the method is not as general as

(1) Presented before the Division of Organic Chemistry at the Baltimore meeting of the American Chemical Society, April, 1939.

(2) Stephen, *J. Chem. Soc.*, 127, 1874 (1925).

claimed. Stephen states, "the method is applicable to aliphatic and aromatic nitriles, and the yields are usually almost quantitative." Exceptions are made by Stephen only in the cases of *o*-tolualdehyde and α -naphthaldehyde, where "steric hindrance" is offered as an explanation for poor yields.

The method has been tried in this Laboratory with good results in the preparation of benzaldehyde, *p*-tolualdehyde and β -naphthaldehyde, and with only fair results in the preparation of phenylacetaldehyde and isocaproaldehyde. Stephen's poor yields with α -naphthaldehyde and *o*-tolualdehyde have been verified, and the method has been found completely unsatisfactory for the preparation of β -hydroxypropionaldehyde.

Experimental

Preparation of Phenylacetaldehyde.—Eleven runs were made, each different, and the following was found to give the highest yield.

A mixture of anhydrous stannous chloride (57 g., 0.3 mole, prepared by heating the hydrated salt for one hour in a 200° bath, cooling and pulverizing the resulting solid mass) and dry ether (400 ml., twice distilled from sodium) was placed in a 2-liter three-necked round-bottomed flask, provided with a mechanical stirrer and a reflux condenser fitted with a calcium chloride drying tube. The mixture was saturated with dry hydrogen chloride,³ using slow stirring to agitate the stannous chloride. Within two hours all of the solid stannous chloride had dissolved, forming a separate lower viscous layer.

The source of hydrogen chloride was then disconnected and phenylacetonitrile (16 g., 0.136 mole, freshly distilled) was added rapidly by means of a dropping funnel. The mixture was stirred vigorously for one hour and then allowed to stand for eighteen hours. The aldimine hydrochloride-stannic chloride complex began to separate after five hours.

The ethereal hydrogen chloride was removed by decantation and the residue washed twice with 100-ml. portions of dry ether to remove hydrogen chloride. To the residue were added 800 ml. of water and sufficient solid sodium bicarbonate to render the solution neutral to congo red.

(3) "Organic Syntheses," Coll. Vol. I, p. 287 (1932).