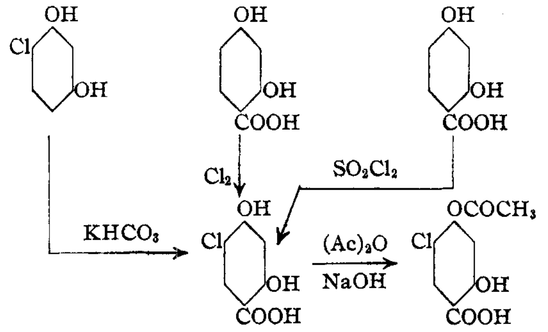
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ALBERTA]

Orientation in the Benzene Ring. The Preparation of 5-Chloro-β-resorcylic Acid[1]

BY R. B. SANDIN AND R. A. MCKEE

During some work which has been in progress on the mercuration of resorcinol derivatives, it was necessary to prepare 5-chloro-β-resorcylic acid. Fabre[2] chlorinated β-resorcylic acid in ether solution with sulfuryl chloride and obtained what he called 2,4-dihydroxy-3-chlorobenzoic acid melting at 203°. He also heated 4-chlororesorcinol with potassium bicarbonate and obtained what he called 2,6-dihydroxy-3-chlorobenzoic acid melting at 215–216°. Finally Hemmelmayr and Meyer[3] chlorinated β-resorcylic acid directly in hot glacial acetic acid solution and obtained what they called 5-chloro-2,4-dihydroxybenzoic acid, melting at 175°. It would appear then that there is the possibility of obtaining three isomeric monochlorodihydroxybenzoic acids, depending upon the above procedures. In an attempt to repeat this work, the conclusion arrived at was that the three acids described are the same and that they all correspond to Hemmelmayr's 5-chloro-2,4-dihydroxybenzoic acid, but with a higher melting point.



To characterize a compound of this type by its melting point alone might lead to certain difficulties. Attention is called to the fact that β-resorcylic acid is recorded in the literature as having at least seven different melting points.[4] For that reason the compounds produced by the above procedures were converted into their monoacetates by the method of Lesser and Gad.[5] These monoacetates were then shown to be identical by mixed melting point determinations. The formation of a monoacetate also establishes the fact that the carboxyl group in that acid which is prepared by the action of potassium bicarbonate on 4-chlororesorcinol, must be in the ortho-para position with respect to the two hydroxyl groups. The work of Lesser and Gad clearly indicates that the acetylation of hydroxycarboxylic acids with acetic anhydride in aqueous alkaline solution is a general reaction except when the hydroxyl group is in the ortho position to the carboxyl group.

Rice[6] observed that a mixture of monobromo and dibromo acids was invariably obtained, when β-resorcylic acid (1 mole) was brominated directly with bromine (1 mole). Rice also found that the two acids in the mixture could be separated by fractional crystallization from solvents, only with considerable difficulty. The authors have found this to be the case also in the direct chlorination of β-resorcylic acid. This may account for the low melting point reported by Hemmelmayr and Meyer.[3]

As a result of this work it is considered that the best procedure for the preparation of 5-chloro-β-resorcylic acid is by the action of sulfuryl chloride on β-resorcylic acid in acetic acid solution.

Experimental Part

Preparation of 5-Chloro-β-resorcylic Acid

Method 1.—4-Chlororesorcinol was heated with potassium bicarbonate in aqueous solution. The acid produced by acidifying with hydrochloric acid was repeatedly crystallized from boiling water and dried at 100° for four hours until it had a constant m. p. of 224–225° (corr.) with dec. and gave on analysis the correct chlorine content.

Acetylation by the method of Lesser and Gad gave 2-hydroxy-4-acetoxy-5-chlorobenzoic acid, which was crystallized from dilute alcohol, forming long colorless needles; m. p. 169° (corr.).

Anal. Calcd. for $C_9H_7O_5Cl$: Cl, 15.40. Found: Cl, 15.37, 15.38.

Method 2.—β-Resorcylic acid was chlorinated with sulfuryl chloride in glacial acetic acid solution. The acid produced was purified in the above manner, melted at 224–225° (corr.) with dec. and gave the right chlorine content. It gave a monoacetate of m. p. 169° (corr.).

Anal. Calcd. for $C_9H_7O_5Cl$: Cl, 15.40. Found: Cl, 15.30, 15.41.

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(1) This work was supported in part by funds from the Carnegie Corporation Research Grant, for which the authors express their thanks.

(2) Fabre, *Ann. chim.*, **18**, 49–116 (1922).

(3) Hemmelmayr and Meyer, *Monatsh.*, **46**, 143–156 (1926).

(4) Bistrzycki and Kostanecki, *Ber.*, **18**, 1983 (1885); "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1926, Vol. I, p. 209; Nierenstein and Clibbens, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1930, Vol. X, p. 95.

(5) Lesser and Gad, *Ber.*, **59B**, 233–236 (1926).

(6) Rice, THIS JOURNAL, **48**, 3125 (1926).

Method 3.—β-Resorcylic acid (1.0 mole) in glacial acetic acid was chlorinated with chlorine (1.0 mole) also in glacial acetic acid. The acid produced always contained some dichloro compound as shown by analysis. This was removed by refluxing the reaction mixture in aqueous solution for several hours. Under these conditions the dichloro acid decomposes more rapidly than the monochloro acid to give the dichlororesorcinol, which is very soluble in water. The acid obtained melted at 223–224° (corr.) with dec. The monoacetate melted at 169° (corr.).

Anal. Calcd. for $C_9H_7O_5Cl$: Cl, 15.40. Found: Cl, 15.30, 15.38.

Mixed melting point determinations which were carried out on the acids and their monoacetates prepared by the above procedures, showed no depression in the melting points.

On certain occasions it was noticed that the 5-chloro-β-resorcylic acid crystallized from water as a mixture of needle-like and granular crystals. On standing the former type of crystal gradually changed into the granular type, which was the common one. It was also noticed that the 5-chloro-β-resorcylic acid on being kept for several months had a m. p. of 211–213° (corr.).

Summary

The preparation of 5-chloro-β-resorcylic acid by three different methods has been described.

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Synthetic Fats. I. The Preparation of Trinondecylin[1]

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The study of fats derived from fatty acids containing an odd number of carbon atoms has increased considerably in the last decade, due to the proposed use of such fats in diabetic diets. A thermal investigation of triglycerides, *e. g.*, from the standpoint of "triple melting"[2] is also interesting. Clarkson and Malkin have recently shown that "triple melting" is general for all the triglycerides from tricaprin to tristearin, but whereas the two lower melting points lie on smooth curves, the highest melting points show the property of alternation. The modifications which correspond to the two highest melting points are crystalline modifications, while the lowest melting form, which is obtained by rapid cooling of the molten triglyceride, has the characteristics of a glass.

For these various reasons it was decided to synthesize the triglyceride of nondecylic acid, since there seems to be no information on it in the literature.

Nondecylic acid was made by the following reactions: *n*-octadecyl alcohol ⟶ octadecyl iodide ⟶ octadecyl cyanide ⟶ nondecylic acid. The intermediates were purified, their purity checked by analysis, and it is believed that homologs were eliminated by this process. The fat was made by the method of Verkade, van der Lee and Meerburg.[3] It showed the property of "triple melting" and its highest melting point was lower than the highest melting point of tristearin, thus giving evidence of alternation. The melting points found for the trinondecylin lie fairly well on the extrapolated curves of Clarkson and Malkin, with the exception of the α-form. From a study of the curves, one might expect the melting point of this form to be higher.

Experimental

As a starting material, commercial *n*-octadecyl alcohol,[4] which has been available for some time, was used. Phillips and Mumford[5] have found that the pure *n*-tetradecyl and *n*-octadecyl alcohols which they obtained from the technical varieties agreed closely in properties with those products obtained by the orthodox reduction procedure. The authors have found this to be the case also, for the *n*-octadecyl alcohol. The commercial alcohol was fractionated under reduced pressure (0.5–1 mm.) through a column 100 × 1.3 cm. of Raschig rings, wound with a heating coil and insulated with asbestos. The fraction boiling at 165–170° was crystallized five times from ligroin (b. p. 30–60°). A constant m. p. of 58°[6] was usually obtained after the third crystallization. Smith[7] has reported, m. p. 58.0°, capillary tube 58.5°. Octadecyl iodide was

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[1] This work was supported in part by funds from the Carnegie Corporation Research Grant, for which the authors express their thanks.

[2] Othmer, *Z. anorg. Chem.*, **91**, 240 (1915); Nicolet, *Ind. Eng. Chem.*, **12**, 741 (1920); Loskit, *Z. physik. Chem.*, **134**, 135 (1928); Clarkson and Malkin, *J. Chem. Soc.*, 666 (1934).

[3] Verkade, van der Lee and Meerburg, *Rec. trav. chim.*, **51**, 850 (1932).

[4] The authors are grateful to the E. I. du Pont de Nemours Co., Wilmington, for supplies of "Stenol" (commercial *n*-octadecyl alcohol), and to the Röhm and Haas Co., Philadelphia, for a supply of technical *n*-octadecyl alcohol.

[5] Phillips and Mumford, *J. Chem. Soc.*, 235 (1933).

[6] All melting points recorded are capillary ones.

[7] Smith, *J. Chem. Soc.*, 802 (1931).