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

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

BY D. W. WOOLLEY AND R. B. SANDIN

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).

prepared by the method of Bleyberg and Ulrich.[8] Octadecyl cyanide was prepared according to Levene and Taylor,[9] who have found two melting points for some of the higher cyanides, but say nothing regarding this property for the octadecyl cyanide. In some preliminary work the authors have noticed a lower melting modification of octadecyl cyanide, m. p. 34–34.5°. Further work will be done on the various cyanides from this standpoint. The cyanide was hydrolyzed by boiling with alcoholic sodium hydroxide. It was found that by blowing air through the boiling solution, the hydrolysis was greatly speeded up. The acid obtained was crystallized from alcohol and benzene, m. p. 68–68.5°. Bleyberg and Ulrich[8] have reported m. p. 68–69°, Levene and Taylor,[9] m. p. 69–70°, and very recently, Shiina,[10] m. p. 68.2–68.4°. The neutral equivalent was 300.0; calculated for $C_{19}H_{38}O_2$, 298.3.

Trinondecylin was made from nondecylic acid and glycerol. It was crystallized once from ether, once from alcohol and four times from toluene. The phenomenon of "triple melting" was observed, *viz.*, α, 66.5–67°; β, 70.5°; glass, 60°. The phenomenon of alternation was evident in the case of the β-form. Loskit[2] has reported for β-tristearin, m. p. 71.8°; Clarkson and Malkin,[2] m. p. 71.5°; with the Abbé refractometer, n^{72}_D 1.4430.

Anal. Calcd. for $C_{60}H_{116}O_6$: C, 77.16; H, 12.54. Found: C, 77.11 and 77.50; H, 12.46 and 12.59.[11] The saponification equivalent was 310.8; calcd., 311.0. Alkaline hydrolysis of trinondecylin gave nondecylic acid with the same melting point as the original acid. Trinondecylin was hydrolyzed by lipase.

Summary

The preparation of trinondecylin is described. Trinondecylin occurs as the α, β and glassy modifications melting, respectively, at 66.5–67, 70.5 and 60°. The phenomenon of alternation is evident in the case of the β modification.

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[8] Bleyberg and Ulrich, *Ber.*, **64**, 2504 (1931).

[9] Levene and Taylor, *J. Biol. Chem.*, **59**, 905 (1924).

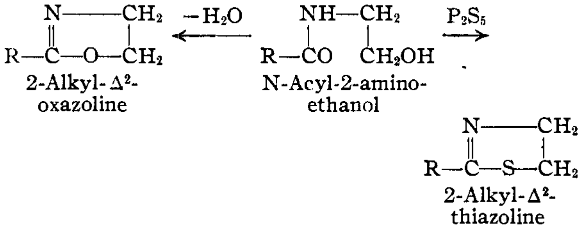
[10] Shiina, *J. Soc. Chem. Ind.*, Japan, **36**, Suppl. binding, 569 (1933).

[11] The authors are indebted to Mr. W. A. Lang for the combustion analysis.

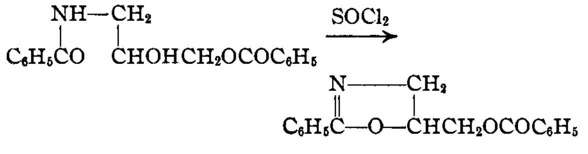
The Synthesis of Δ²-Oxazolines and Δ²-Thiazolines from N-Acyl-2-aminoethanols

BY HENRY WENKER

A study of the chemistry of N-acyl-2-aminoethanols of the formula $RCONHCH_2CH_2OH$ was considered of interest with regard to possible heterocyclic syntheses according to the scheme



Bergmann and Brand[1] have described the preparation of a Δ²-oxazoline from a N-acyl-2-aminoalcohol



The method has not been used for the preparation of other Δ²-oxazolines, nor does the literature contain any reference concerning the synthesis of a Δ²-thiazoline from a N-acyl-2-aminoalcohol.

Since data on N-acyl-2-aminoethanols, the starting material used for the present investigation, are few and partly not in agreement,[2,3,4] a general method for their preparation seemed desirable. It was found that compounds of this class can be prepared conveniently by heating equimolar proportions of acid and 2-aminoethanol to 200°, followed by vacuum distillation. The acids used were formic, acetic, propionic and benzoic.

Attempts at cyclization showed that the corresponding Δ²-oxazolines can be prepared from N-acetyl- and -propionyl-2-aminoethanol by thermal decomposition, while phosphorus pentoxide is required as condensing agent in the case of the benzoyl compound. N-Formyl-2-aminoethanol, under various experimental conditions, decomposed with evolution of carbon monoxide and regeneration of 2-aminoethanol.

Under the influence of phosphorus pentasulfide, all of the N-acyl-2-aminoethanols under consideration yielded the corresponding Δ²-thiazolines.

Experimental

Materials Used.—2-Aminoethanol was commercial monoethanolamine,[5] boiling within 2°. Formic, acetic

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[1] Bergmann and Brand, *Ber.*, **56**, 1280 (1923).

[2] French Patent 638,023 (1928).

[3] Fränkel and Cornelius, *Ber.*, **51**, 1657 (1918).

[4] Knorr, *ibid.*, **36**, 1278 (1903).

[5] From Carbide and Carbon Chemicals Corporation.