sulfonate was heated on a water-bath for two and one-half hours with stirring. The chloroethoxy compound was separated from unaltered ester by shaking with a minimum quantity of petroleum ether. The yield was 75%, and the compound melted at $64-65^{\circ}$ after crystallization from 95% ethanol.

Anal. Calcd. for $C_{14}H_{11}O_2C1$: Cl, 14.38. Found: Cl, 14.53 and 14.51.

4- β -Diethylaminoethoxydibenzofuran, $C_{12}H_7O[OCH_2-CH_3N(C_2H_5)_2]$, was prepared in a 22% yield by heating the chloroethoxy compound with diethylamine at 100° for eighteen hours. The impure base could not be distilled without significant decomposition. The hydrochloride formed by passing hydrogen chloride into a dry etheracetone solution precipitated as an oil which crystallized after standing for several days and melted at 128.5–129.5° on crystallization from an ether-acetone solution.

Anal. Calcd. for $C_{18}H_{22}O_2NCl$: N, 4.38. Found: N, 4.32 and 4.48.

4- β -Piperidinoethoxydibenzofuran, C₁₂H₇O(OCH₂CH₂-NC₈H₁₀), was prepared by heating the chloroethoxy compound with piperidine on a steam-bath for twenty-four hours. The yield was 52%. The free amine distils at 213° (2 mm.) and the hydrochloride melts at 210.5–212°.

Anal. Calcd. for $C_{19}H_{22}O_2NCl$: N, 4.22. Found: N, 4.44 and 4.56.

4-Dibenzofurancarboxylic Acid Chloride, $C_{12}H_7$ -OCOCl.—The 4-dibenzofurancarboxylic acid was prepared in 30% yield by carbonation of 4-dibenzofuryl-lithium (prepared, in turn, through *n*-butyl-lithium and dibenzofuran); and in 50% yield by carbonating 4-dibenzofurylsodium. A quantitative yield of the crude acid chloride was obtained from 112 g. (0.52 mole) of 4-dibenzofurancarboxylic acid and 500 g. (4.2 moles) of thionyl chloride. The acid chloride was crystallized from ethanol, and finally purified by sublimation to melt at 118°.

Anal. Calcd. for $C_{13}H_7O_2Cl$: Cl, 15.22. Found: Cl, 15.24 and 15.11.

4-Dibenzofurancarboxylic acid amide was prepared by W. G. Bywater from the acid chloride and ammonium hydroxide, and melted at $181-182^{\circ}$ after crystallization from ethanol.

Anal. Calcd. for $C_{13}H_9O_2N$: N, 6.63. Found: N, 6.73 and 6.46.

4-Aminodibenzofuran. (a) From 4-Hydroxydibenzofuran.—A mixture of 2.3 g. (0.0125 mole) of 4-hydroxydibenzofuran, 6 g. of fused zinc chloride and 2 g. of ammonium chloride was heated in a sealed tube at 275–280° for twenty-one hours. The brown mass was removed from the tube by lixiviating with dilute hydrochloric acid and ether. The acid solution was neutralized with sodium hydroxide and then extracted with ether. Hydrogen chloride then gave the amine hydrochloride in a 16% yield. The free amine, obtained from the hydrochloride by dil. alcoholic ammonium hydroxide, melts at 84.5–85.5°.

Anal. Calcd. for $C_{12}H_{9}ON$: N, 7.65. Found: N, 7.72 and 7.46.

(b) From 4-Dibenzofurancarboxylic Acid.—A Hofmann reaction on the amide of 4-dibenzofurancarboxylic acid gave yields of the amine ranging from 30 to 50%. The procedure was patterned after that described by Goldschmiedt⁴ with 4-fluorenonecarboxylic acid amide.

Both preparations of the 4-amine were made by W. G. Bywater.

4-Acetaminodibenzofuran.—A benzene solution of 4aminodibenzofuran was acetylated by acetic anhydride to give an 89% yield of the 4-acetamino compound melting at 172.5° .

Anal. Calcd. for $C_{14}H_{11}O_2N$: N, 6.22. Found: N, 6.16 and 6.21.

Summary

Some amino derivatives have been prepared in connection with the physiological properties of dibenzofurans.

(4) Goldschmiedt, Monatsh., 28, 890 (1902).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DEPAUW UNIVERSITY]

Homoamines and Homoacids¹

BY PERCY L. JULIAN AND BERNARD M. STURGIS

This paper records details of a simple, relatively inexpensive and rapid method for preparation in good yield of β -arylethylamines (V) and arylacetic acids (VI), substances which are oftneeded tools in any laboratory, and especially one devoted to a study of natural products. The procedure has been employed successfully for preparation of homoveratrylamine, homopiperonylamine, homoanisylamine and the correspond-

(1) Abstracted from the senior research of Bernard M. Sturgis at DePauw University and read before the American Chemical Society at the fall meeting in Chicago, 1933. ing homoacids, and indeed appears generally applicable.

The substituted benzaldehydes, which constitute starting material, are condensed with rhodanine in the initial reaction, and the remaining steps are indicated by formulas (I) \longrightarrow (VI).

Condensation reactions of aldehydes with rhodanine have been beautifully worked out by Gränacher and his collaborators,² but these useful reactions have been overlooked as methods for

(2) Gränacher et al., Helv. Chim. Acta, 5, 610 (1922); 6, 458 (1923).



obtaining homoamines and acids, probably because of the prevailing cost of rhodanine. The rhodanine preparation recorded in this paper³ removes this difficulty. The decarboxylation and dehydration of oximino acids like (III) has also escaped careful study, but is effected with excellent yields through mere warming in acetic anhydride.

Since the method leads to homonitriles, it is identical in its last stages with the procedure employed by Hahn and Schales⁴ for converting these substances into the corresponding homoamines and acids, but was communicated to the Society before the papers of these authors appeared.

Experimental Part

The Preparation of Rhodanine.-Dry ammonia gas is passed for three and one-half hours into a mixture of 250 g. of carbon bisulfide, 200 cc. of alcohol and 200 cc. of ether, cooled well in a freezing mixture. The contents of the flask then represent an almost solid cake of pale yellow crystals of ammonium dithiocarbamate. These are filtered by suction, washed well with 50 cc. of cold alcohol, followed by 100 cc. of ether. The material must be used immediately; on standing it deteriorates rapidly. In the meantime a solution of sodium chloroacetate has been prepared by adding a solution of 98 g. of sodium hydroxide in 150 cc. of water to a solution of 238 g. of chloroacetic acid (Eastman practical) in 200 cc. of water. Sodium carbonate is added until the solution is neutral to litmus. To the solution thus prepared the ammonium dithiocarbamate, which should weigh 280-310 g. is added gradually, under stirring and good cooling, the color turning dark at first, gradually lightening and finally becoming a straw yellow if all has gone well. This solution is then added under stirring to 300 cc. of concentrated hydrochloric acid which has been heated to 80-90°. The rhodanine slowly separates in glistening, pale yellow prisms. After an hour's standing the flask with its contents is cooled in an icebath, the rhodanine filtered and washed well with water; yield of air-dried material 210-230 g., m. p. 162°. This

rhodanine is pure enough for practically all condensations, but may be purified by recrystallization from alcohol, m. p. 170°, almost colorless.

Veratralrhodanine.—To a solution of 100 g. of veratrumaldehyde and 80 g. of rhodanine in 400 cc. of hot glacial acetic acid, 150 g. of fused sodium acetate is added and the whole boiled for one-half hour with occasional shaking. The veratralrhodanine soon separates in orange colored crystals. The whole mass is poured into 3 liters of water, the crystals filtered off, washed well with water, then with little alcohol and ether; yield 162 g., 96% of the theoretical; m. p. 232°, recrystallized from acetone.

Anal. Calcd. for $C_{12}H_{11}O_3S_2N$: C, 51.24; H, 3.91. Found: C, 51.54; H, 4.21.

Cleavage of Veratralrhodanine with Alkali.-Forty-four grams of veratralrhodanine is suspended in 200 cc. of 15%sodium hydroxide and heated on a vigorously boiling water-bath with occasional shaking until all the material dissolves (about one-half hour). The alkaline solution is cooled well in a freezing mixture and the acid precipitated rapidly with 200 cc. of 10% hydrochloric acid. It is well not to add the acid too slowly, for the material which first precipitates goes back into solution and the yield is lowered. Slow addition necessitates use of more than the quantity of acid indicated above, and several runs have shown that this quantity is more than sufficient. If the precipitate which first comes out is allowed to go back into solution, additional acid precipitates a gum which crystallizes with difficulty and a considerable quantity of hydrogen sulfide is evolved. The amorphous acid which separates soon crystallizes on standing in the freezing mixture to a pale yellow powder; yield practically quantitative, m. p. 179° after recrystallization from methyl alcohol. For the best results it is not recommended to run larger quantities for the cleavage. Indeed smaller runs are to be preferred, especially since the process is simple and several runs can be made simultaneously. The succeeding operations go well with any quantities.

Anal. Calcd. for $C_{11}H_{12}O_4S$: C, 55.0; H, 5.0. Found: C, 54.8; H, 4.7.

 α -Oximino- β -3,4-dimethoxyphenylpyruvic Acid.—To a solution of sodium ethylate prepared from 22.5 g. of sodium and 650 cc. of ethyl alcohol is added a warm solution of 67.5 g. of hydroxylamine hydrochloride in 60 cc. of water. The solution of hydroxylamine is filtered from the precipitated sodium chloride and poured onto 75 g. of the thicketo acid (V) once recrystallized from methyl alcohol. The resulting solution is heated on the water-bath for about twenty minutes and the alcohol removed under diminished pressure. The residual solid mass is dissolved in 160 cc. of 5% sodium hydroxide, filtered from sulfur, well cooled and cautiously acidified with 150 cc. of 10%hydrochloric acid. On scratching the oximino acid crystallizes in almost colorless flakes. It is filtered, washed with 200 cc. of water and dried in a vacuum desiccator over potassium hydroxide overnight; yield 72 g., identical with the product described by Kropp and Decker.⁵

Decomposition of α -Oximino- β -3,4-dimethoxyphenylpyruvic Acid to 3,4-Dimethoxyphenyl-acetonitrile.— Ninety-three grams of crude dry oximino acid is sus-

⁽³⁾ Cf. Holmberg, J. prakt. Chem., [2] 79, 265 (1909); 81, 451 (1910).

⁽⁴⁾ Hahn and Schales, Ber., 68, 24 (1935).

⁽⁵⁾ Kropp and Decker, ibid., 42, 1184 (1909).

pended in 300 cc. of acetic anhydride and warmed cautiously. Effervescence begins on slightest warming and the oximino acid gradually goes into solution. After all decomposition is over, the acetic anhydride is removed under diminished pressure and the residue taken up in water and ether. The ethereal layer is washed well with sodium carbonate and distilled. At 187–188° an almost colorless liquid distils, yield 65 g. This represents almost pure nitrile and crystallizes on cooling, m. p. 64–65°.⁴ For the catalytic hydrogenation to homoveratrylamine it is recrystallized once from methyl alcohol.

All these reactions have been carried out on piperonal and anisaldehyde and yield equally as good results.

The senior author is grateful to his sister, Irma, for the preparation of large quantities of rhodanine in the early stages of the work, to the Rosenwald Fund for a grant assisting us in these and other investigations, and to Dean W. M. Blanchard, Head of the Department, for his continued enthusiastic support.

Summary

1. The facile preparation of rhodanine in large quantity is described in detail.

2. Through condensation of rhodanine with veratrum aldehyde, anisaldehyde and piperonal, the corresponding homoacid nitriles, RCH₂CN, have been prepared in excellent yield.

3. Obtention of these nitriles offers a simple and easily consummated route to the corresponding homoamines and homoacids.

GREENCASTLE, INDIANA RECEIVED APRIL 22, 1935

[CONTRIBUTION NO. 47 FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF UTAH]

Boranilide

BY CORLISS R. KINNEY AND DONALD F. PONTZ

In 1920, Chaudhuri¹ prepared a substance which he named boranilide, $C_{\delta}H_{\delta}NHBO$, by heating aniline and boric acid with anhydrous zinc chloride. The compound is particularly interesting because it is one of the few derivatives of metaboric acid to be reported.

Upon following Chaudhuri's directions for making boranilide the product crystallized from alcohol in needles and "did not melt at 212°" as Chaudhuri described the substance. The actual melting point of the product is 255° and when it was investigated further was found not to be a boron compound, but a zinc compound which was readily identified as the known double salt of aniline and zinc chloride, (C6H5NH)2.ZnCl2.2 Since Chaudhuri did not give the melting point of his product it is impossible to state whether or not his product which he called boranilide was the compound of aniline and zinc chloride which we obtained and identified, but we are convinced that the directions which he gave for preparing boranilide yield only the double salt of aniline and zinc chloride. Furthermore, his directions for purifying the crude product require that it be successively extracted with small quantities of water, washed with very dilute hydrochloric acid, and repeatedly washed with warm water before finally recrystallizing the substance from alcohol. Such treatment is astounding for a derivative of metaboric acid, which should, at least, be hydrated by such methods. The properties of boranilide should be related to those of the esters of boric acid on the one hand and to those of the organoboron oxides on the other, in which series of compounds the boronyl group —BO is attached successively to carbon, nitrogen and oxygen.

RBO RNHBO ROBO or (RO)3B

The organoboron oxides are readily hydrated in contact with water to the corresponding organoboric acid and are hydrolyzed by boiling water or, more rapidly, by hot alkalies.

$$RBO + HOH \longrightarrow RB(OH)_2 + HOH \longrightarrow RH + (HO)_3B$$

The esters of metaboric acid, at the other end of the series are, unfortunately, unknown, which fact may be significant in itself. However, if the ortho esters may be used for comparison, we have substances which are instantly hydrolyzed by cold water.

 $(RO)_{3}B + 3HOH \longrightarrow 3ROH + (HO)_{3}B$

Chaudhuri gave a number of reactions for his compound and since it is possible that he had the double salt of aniline and zinc chloride, which we obtained by following his directions, we have applied his reactions to the product which we obtained. With benzoyl chloride Chaudhuri obtained a derivative melting at 166°. The double

⁽¹⁾ Chaudhuri, J. Chem. Soc., 117, 1081 (1920).

⁽²⁾ Howard and Stimpert, THIS JOURNAL, 45, 3106 (1923).