

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° after crystallization from 95% ethanol.

Anal. Calcd. for $C_{14}H_{11}O_2Cl$: Cl, 14.38. Found: Cl, 14.53 and 14.51.

4- β -Diethylaminoethoxydibenzofuran, $C_{12}H_{17}O(OCH_2CH_2N(C_2H_5)_2)$, 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 ether-acetone 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 $C_{15}H_{22}O_2NCl$: N, 4.38. Found: N, 4.32 and 4.48.

4- β -Piperidinoethoxydibenzofuran, $C_{12}H_{17}O(OCH_2CH_2NC_5H_{10})$, was prepared by heating the chloroethoxy compound with piperidine on a steam-bath for twenty-four hours. The yield was 52%. The free amine distills 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, $C_{12}H_7OCOC_2H_5$.—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-dibenzofuryl-sodium. 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° 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 $C_{12}H_9ON$: 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-fluorenoncarboxylic acid amide.

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

4-Acetaminodibenzofuran.—A benzene solution of 4-aminodibenzofuran 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.*, **23**, 890 (1902).

AMES, IOWA

RECEIVED APRIL 22, 1935

[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 oft-needed 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) \rightarrow (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).

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 distills, 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, RCH_2CN , 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

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[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_6H_5NHBO , 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, $(C_6H_5NH)_2 \cdot ZnCl_2$.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.

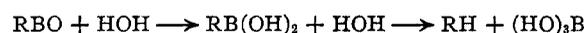
(1) Chaudhuri, *J. Chem. Soc.*, **117**, 1081 (1920).

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

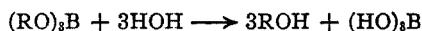
Such treatment is astounding for a derivative of metaboric acid, which should, at least, be hydrated by such methods. The properties of boranilide should be related to those of the esters of boric acid on the one hand and to those of the organoboron oxides on the other, in which series of compounds the boronyl group $-BO$ is attached successively to carbon, nitrogen and oxygen.



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 alkalis.



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.



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