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, 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.

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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, Chaudhuri[1] 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. 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.

$$RBO \quad RNHBO \quad ROBO \text{ or } (RO)_3B$$

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.

$$(RO)_3B + 3HOH \longrightarrow 3ROH + (HO)_3B$$

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

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

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

salt when treated in a similar manner gave benzanilide melting at 160–161° which was identified by a mixed melting point determination. With bromine Chaudhuri obtained ortho, meta and para derivatives, the latter melting at 121–122°. From the double salt only one substance was obtained melting at 118–120°. It was identified by a mixed melting point determination to be tribromoaniline, melting at 119°. With nitrous acid Chaudhuri obtained a compound melting at 83°, but we were unsuccessful in obtaining a similar compound. As would be expected, the dark colored liquid product smelled strongly of phenol. The other reactions described by Chaudhuri also failed to yield crystalline products. Consequently, since we were unable to duplicate entirely Chaudhuri's results, we are not able to state that Chaudhuri had the double salt of aniline and zinc chloride. On the other hand, Chaudhuri's directions for making boranilide most certainly yield the double salt of aniline and zinc chloride.

Experimental Part

The Reaction of Aniline, Boric Acid and Zinc Chloride.—Chaudhuri's procedure for making boranilide was followed exactly. The product crystallized from alcohol as Chaudhuri stated, and was soluble in dilute acids and bases. The substance melted at 255°. Variations in the procedure were made, but in each case the same substance was obtained. Also, the same compound was obtained when the boric acid was omitted.

The compound prepared with boric acid gave only a faint flame test for boron. When burned a residue remained which evolved hydrogen chloride upon treatment with concentrated sulfuric acid. An alcoholic solution of the substance when treated with an alcoholic solution of sodium sulfide gave a copious precipitate of zinc sulfide, insoluble in water. The substance was analyzed for chlorine by the Carius method and gave the following results.

Anal. Calcd. for $(C_6H_5NH_2)_2 \cdot ZnCl_2$: Cl, 22.04. Found: Cl, 22.11, 21.91.

The Reaction with Benzoyl Chloride.—The directions given by Chaudhuri for benzoylating boranilide were applied to the double salt. The product melted low and contained some benzoic acid which was readily removed by extraction with sodium hydroxide. The product was washed with water and dried. It then melted at 160–161°. The melting point was not lowered by mixing the substance with pure benzanilide.

The Reaction with Sulfur.—The double salt was heated with flowers of sulfur, again following Chaudhuri's directions. Upon extracting the product with warm carbon bisulfide a black residue remained which did not melt when heated as high as 270°. The melting point given for thioboranilide is 109–110°.

Reaction with Nitrous Acid.—Chaudhuri's directions for making nitrosoboranilide gave with the aniline salt a red-brown liquid product which did not yield crystals melting at 83°. The oil had, however, the unmistakable odor of phenol.

Reaction with Bromine.—Following Chaudhuri's directions for brominating boranilide a substance was obtained which dissolved completely in chloroform, leaving no white residue. Upon evaporating the chloroform, silky needles melting at 118–120° were obtained instead of Chaudhuri's *o*-bromoboranilide melting at 82°. The silky needles were identified by a mixed melting point determination to be tribromoaniline, melting at 119°. The white residue which we did not get gave Chaudhuri *p*-bromoboranilide, melting at 121–122°.

Chaudhuri prepared *m*-bromoboranilide by brominating boranilide in a sulfuric acid solution. The aniline compound did not yield a crystalline product under similar conditions.

Summary

Following Chaudhuri's directions for making boranilide, the double salt of aniline and zinc chloride was obtained. Since Chaudhuri did not give the melting point of "boranilide," it is not possible to be certain that Chaudhuri had the aniline-zinc compound. However, the reactions which he gave for boranilide may be interpreted at least in part, on the assumption that he had the double salt of aniline and zinc chloride.

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