

sodium bisulfite and finally with water. The residue from evaporation of the solvent was crystallized from chloroform in plates, m. p. 216–218°. A mixed melting point with an authentic sample of 3-hydroxy-*etio*-bilianic acid gave no depression. A yield of 110 mg. of pure product was obtained.

*Anal.* Calcd. for  $C_{19}H_{30}O_5$ : C, 67.4; H, 8.9. Found: C, 67.1; H, 9.0.

When refluxed with acetic anhydride and sublimed in high vacuum, the sublimate gave a product which was crystallized from ether-pentane in small prisms, m. p. 198–201°. This gave no depression in melting point when

mixed with an authentic sample of the acetate anhydride of 3( $\beta$ )-hydroxy-*etio*-bilianic acid.

*Anal.* Calcd. for  $C_{21}H_{30}O_5$ : C, 69.6; H, 8.3. Found: C, 69.7; H, 8.4.

### Summary

The structure assigned by Fieser and Jacobsen<sup>1</sup> to the potassium permanganate oxidation product of anhydrosarsasapogenoic acid is shown to be wrong. We suggest a new structure of this acid.

STATE COLLEGE, PENNA. RECEIVED SEPTEMBER 22, 1941

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## The Use of Bunte Salts in Synthesis. III. The Preparation of Aliphatic Disulfides<sup>1</sup>

BY HARRY E. WESTLAKE, JR.,<sup>2</sup> AND GREGG DOUGHERTY

Sodium alkylthiosulfates, or Bunte salts, have been reported to form disulfides readily by pyrolysis,<sup>3</sup> electrolysis,<sup>4</sup> reaction with iodine,<sup>5</sup> and reaction with hydrogen peroxide.<sup>6</sup> Of these methods, the last two appeared to give the most satisfactory results. However, their discoverers prepared only a few disulfides, none of which were normal alkyl compounds. We have undertaken, therefore, the preparation of representative members of this latter type, and have obtained varying, but, on the whole, good yields. To the compounds previously prepared by the iodine reaction, namely, benzyl and *o*-nitrobenzyl disulfides and dimethyl dithioglycolate, we have added butyl, heptyl, octyl, dodecyl, and octadecyl disulfides. Twiss had prepared benzyl, *o*-nitrobenzyl, *p*-nitrobenzyl, and allyl disulfides by the peroxide reaction. To these we have added butyl, heptyl, octyl and dodecyl disulfides. The method appears to be an excellent one for any radical whose Bunte salt can be easily formed.

The intermediate stages of these reactions appear to be highly complicated. As Price and Twiss pointed out,<sup>4</sup> the mechanism probably does not consist of hydrolysis to the mercaptan and the subsequent oxidation of that compound. We have made a study of the process and hope to publish the results in a later paper.

(1) Previous papers: Westlake and Dougherty, *THIS JOURNAL*, **63**, 658 (1941); Stoner and Dougherty, *ibid.*, **63**, 987 (1941).

(2) Now at the Mellon Institute of Industrial Research, Pittsburgh, Pa.

(3) Bunte, *Ber.*, **7**, 646 (1874).

(4) Price and Twiss, *J. Chem. Soc.*, **91**, 2021 (1907); **93**, 1395, 1401 (1908).

(5) Price and Twiss, *ibid.*, **95**, 1489 (1909).

(6) Twiss, *ibid.*, **105**, 36 (1914).

### Experimental

The procedure used was that of Price and Twiss with some modifications due to the liquid nature of certain of the products. The Bunte salt solution was prepared in the usual manner<sup>7</sup> and then either iodine was added in small portions until the color remained, or cooled and allowed to stand with peroxide. The liquid products were extracted with ether; the extract was then evaporated and the residual oil distilled under a vacuum. When the product was solid, it was crystallized from alcohol or acetic acid. If economy is desired, the iodine can be recovered by passing chlorine through the aqueous layer after separation of the product.<sup>8</sup>

***n*-Butyl Disulfide.**—Thirty-eight and one-tenth grams (0.3 mole) of *n*-butyl bromide and 74.4 g. (0.3 mole) of sodium thiosulfate were dissolved in a mixture of 225 cc. of alcohol and 225 cc. of water. The mixture was refluxed until the solution was homogeneous. Then iodine crystals were added in small portions until the color remained. The mixture was transferred to a separatory funnel and the water layer drawn off and extracted with ether. The extract was evaporated and the residual oil was combined with the rest of the product. This was washed with aqueous sodium bisulfite to remove iodine and then dried with sodium sulfate. It boiled at 90–100° (3 mm.),<sup>9</sup> yield 57%.

When the hydrogen peroxide reaction was used, the Bunte salt solution was cooled and allowed to stand at 5° with 40 cc. of 30% hydrogen peroxide and a few drops of dilute sulfuric acid as a catalyst. After several days the product was isolated as before, yield 56%.

***n*-Heptyl Disulfide.**—This compound was prepared by the same procedure used for butyl disulfide; yield, by the iodine reaction, 66%; by the peroxide reaction, 65%; boiling point 143–147° (5 mm.). Since this compound could not be found in the literature, it was analyzed. Calcd. for  $C_{14}H_{28}S_2$ : S, 24.81. Found: S, 24.87.

(7) See the first paper of this series, Westlake and Dougherty, *THIS JOURNAL*, **63**, 658 (1941).

(8) See Mellor, "Treatise on Inorganic Chemistry," Vol. II, p. 41.

(9) Hunter and Sorenson, *THIS JOURNAL*, **54**, 3364 (1932).

*n*-Octyl Disulfide.—The same methods were used for this compound: boiling point 178–183° (5 mm.); yield, by the iodine reaction, 69%; by the peroxide reaction, 52%. It also is a new compound. *Anal.* Calcd. for  $C_{18}H_{34}S_2$ : S, 22.10. Found: S, 22.04.

Lauryl Disulfide.—This compound melts just a little above room temperature (34.5°)<sup>10</sup> and special handling was necessary. The procedure was similar at the start, although a greater amount of time was necessary to form the Bunte salt. After the iodine was added, the liquid product, already tending to solidify, was crystallized from alcohol with a charcoal treatment; yield 35%; melting point 33–34°. In using the peroxide reaction, it was found that the lauryl Bunte salt was not soluble in cold aqueous alcohol. It was therefore filtered off and dissolved in aqueous 1,4-dioxane. The peroxide and acid were added. After the mixture had been allowed to stand in the cold for several days, the product appeared slowly as a solid. It was filtered and recrystallized from alcohol. This appears to be the better way to prepare the compound as the crude product was nearly pure, yield 70%.

*n*-Octadecyl Disulfide.—Eight and one-half grams of octadecyl bromide (prepared after "Organic Syntheses," Vol. XV, p. 24) was dissolved in 25 cc. of alcohol and mixed

(10) Fore and Bost, *THIS JOURNAL*, **59**, 2557 (1937).

with a solution of 5 g. of sodium thiosulfate in 15 cc. of water. After refluxing together for eight to ten hours, iodine was added until the color remained. Then about 50 cc. of a sodium bisulfite solution was added to remove the excess iodine. After filtration, the white product was recrystallized repeatedly from glacial acetic acid and from alcohol, using charcoal in some instances. The melting point remained constant at 54–56°. The compound is reported<sup>10</sup> to melt at 62°, while octadecyl alcohol melts at 59°. It appeared that a trace of the alcohol contaminated the product, and because of the great similarity between the two, could not be removed. This is borne out by the fact that the sulfur analysis is only a fraction of a per cent. low, yield about 49%. *Anal.* Calcd. for  $C_{36}H_{76}S_2$ : S, 11.24. Found: S, 10.80.

### Summary

Present knowledge of the scope of the reactions of Bunte salts with iodine and with hydrogen peroxide as preparative methods has been extended to include the preparation of normal alkyl disulfides. Two of those prepared are new compounds.

PRINCETON, NEW JERSEY RECEIVED OCTOBER 28, 1941

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## Hydrogenation of $\beta$ -Iminonitriles

BY HOMER ADKINS AND GERALD M. WHITMAN<sup>1</sup>

Since imines have been hydrogenated under milder conditions than have nitriles,<sup>2</sup> it seemed probable that aminonitriles, as well as diamines, could be obtained by the hydrogenation of iminonitriles. Only  $\beta$ -iminonitriles are available so that the present study has been confined to this type of compound.<sup>3</sup> Five iminonitriles of the type  $RCH_2C=NHCHRCN$  were prepared by the Thorpe reaction from  $RCH_2CN$  where R was hydrogen, methyl, ethyl, *n*-propyl or phenyl.

All attempts, using Raney nickel or copper chromite as catalysts, to hydrogenate these compounds to  $\beta$ -aminonitriles were unsuccessful. Ether, ethanol, dioxane and methylcyclohexane were used for the reaction medium. The hydrogenations were attempted at temperatures from 75 to 245°. The amount of hydrogen allowed to react was varied from 0.1 to 1.0 mole per mole of iminonitrile. In all cases the iminonitrile was re-

covered unchanged from the reaction mixture, along with various amounts of diamine and cleavage products which were formed as the result of the reaction of three or more moles of hydrogen per mole of iminonitrile.

The complete hydrogenation of the five iminonitriles took place readily over Raney nickel. Where R was methyl, ethyl or propyl, the diamine  $RCH_2CHNH_2CHRCH_2NH_2$  was isolated in yields of 60 to 70% after hydrogenation for two to three hours at 130–150°. Where R was H, the yield of diamine,  $CH_3CHNH_2CH_2CH_2NH_2$ , isolated was lower (41%). Where R was phenyl the yield of the diamine  $C_6H_5CH_2CHNH_2CH(C_6H_5)CH_2NH_2$  was low (27%); because of the tendency for cleavage, the chief product (50% yield) was the monamine  $C_6H_5CH_2CHNH_2CH(C_6H_5)CH_3$ .<sup>4</sup>

The iminonitriles where R was H,  $CH_3$ ,  $C_2H_5$  or  $C_3H_7$  also gave primary amines, containing one less carbon than the iminonitrile, in yields of 7 to 15%. For example,  $CH_3C=NHCH_2CN$  gave

(1) Du Pont Fellow 1939–1940.  
(2) Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937, p. 55.

(3) Bruylants [*Bull. soc. chim. Belg.*, **33**, 307 (1923)] reported the synthesis of  $C_6H_5C=NH(CH_2)_2CN$ , the only compound of a type described in the literature in which the imino group is not  $\beta$  to the cyano group. We were unable to duplicate Bruylant's synthesis.

(4) For the purpose of comparison this amine was prepared by the hydrogenation over Raney nickel of  $C_6H_5CH_2COCHC_6H_5CH_3$  in the presence of ammonia, according to the method of Schwiegler and Adkins, *THIS JOURNAL*, **61**, 3499 (1939).