into formaldehyde and hitherto unknown 6-bromohomoveratraldehyde (IV).

The oxime and the semicarbazone are easily prepared from the aldehyde by the usual methods.

Experimental

6-Bromo-methyleugenol Dibromide.—To 100 g. of methyleugenol dissolved in 200 cc. of ether, 60 cc. of bromine is slowly added with mechanical stirring and external cooling. The reaction is over when the escape of hydrogen bromide ceases. The product separates as a crystalline sludge. It is filtered at the pump, washed with sodium carbonate solution and water and, after drying, recrystallized from ether-petroleum ether. An additional quantity of the product may be recovered from the ethereal mother liquors; yield, 137 g.; white crystals of m. p. 77-78°.

Diacetate of 6-Bromo-methyleugenol Glycol.—Sixty-five grams of 6-bromomethyleugenol dibromide dissolved in 325 cc. of glacial acetic acid is refluxed for two hours with 62.5 g. of silver acetate. The solution is filtered to remove the precipitate of silver bromide and excess silver acetate and the filtrate is concentrated *in vacuo*. Water is added to the residue and the oil which separates is extracted with ether. After washing with sodium carbonate solution and water and drying over sodium sulfate, the ether is distilled. The crude 6-bromomethyleugenol glycol diacetate is obtained as an amber-colored viscous oil; yield 46.6 g.

6-Bromo-methyleugenol Glycol.—46.6 grams of the crude diacetate is refluxed for two hours with 373 cc. of an approximately normal alcoholic solution of potassium hydroxide. Most of the alcohol is then removed by distillation, and the residue diluted with water. The glycol separates and is extracted with chloroform. The chloroform solution is washed once with a small quantity of water, dried, and the solvent is distilled. The impure glycol is recrystallized twice from acetone-petroleum ether; yield 27.7 g.; white, silky needles of m. p. 114-116°.

Anal.[3] Calcd. for $C_{11}H_{14}O_4Br$: C, 45.38; H, 5.20; Br, 27.47. Found: C, 45.42; H, 5.17; Br, 27.54.

6-Bromo-homoveratraldehyde.—To 31.6 g. of 6-bromomethyleugenol glycol dissolved in 200 cc. of absolute chloroform, a solution of 50 g. of lead tetraacetate in 300 cc. of chloroform is slowly added with stirring and external cooling. The temperature is not allowed to rise above 25°. After all the tetraacetate has been added, stirring is continued for thirty minutes at room temperature and the solution is left to stand another three hours. It is then washed thoroughly, first with water, then with sodium bicarbonate solution, and again with water. After drying with sodium sulfate, the chloroform is distilled. The product is purified by distillation in a high vacuum; b. p. 140-145° (0.2 mm.). The distillate crystallizes almost instantaneously. It forms white crystals of m. p. 64-65°; yield 13.3 g. For analysis the product is redistilled in high vacuum. The melting point remains unchanged.

Anal. Calcd. for $C_{10}H_{11}O_3Br$: C, 46.33; H, 4.24. Found: C, 46.33; H, 4.27.

The **oxime** gave white, glittering leaflets; m. p. 115-116°.

Anal. Calcd. for $C_{10}H_{12}O_3NBr$: C, 43.80; H, 4.41. Found: C, 43.89; H, 4.52.

The **semicarbazone** is white, glittering leaflets; m. p. 200-202°.

Anal. Calcd. for $C_{11}H_{14}O_3N_3Br$: C, 41.78; H, 4.46. Found: C, 41.66; H, 4.33.

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[3] Microanalysis by Huffman Microanalytical Laboratories, Denver, Colorado.

A Synthesis of Thiophene-2-glyoxal

BY FRANK KIPNIS AND JOHN ORNFELT

During work on the synthesis of polycarbonyl compounds, it was found desirable to prepare thiophene-2-glyoxal. Two methods have been reported in the literature. That of Fujise[1] proceeds rather deviously from 2-acetylthiophene to the nitroso-ketone, hydrolysis to the glyoxal bisulfite, and, finally, hydrolysis to the glyoxal hydrate. The method of Kröhnke and Börner[2] involves the interaction of 2-bromoacetylthiophene with pyridine to the pyridinium bromide, followed by treatment with *p*-nitrosodimethylaniline to give the N-*p*-dimethylaminophenylnitrone of thiophene glyoxal and, ultimately, acid hydrolysis to the glyoxal hydrate.

It has been found possible to go directly from 2-acetylthiophene to anhydrous thiophene-2-glyoxal by oxidation with selenium dioxide, according to the method indicated for the preparation of phenylglyoxal[3] from acetophenone.

Experimental

To a 500-ml., 3-necked interjoint flask fitted with sealed Hershberg stirrer, reflux condenser and thermometer and heated by a "Glas-Col" mantle, was added 320 ml. of dioxane, 11 ml. of water and 55.5 g. (0.5 mole) of powdered selenium dioxide. Stirring and heating at 55° was continued until solution was complete. Sixty-three grams (0.5 mole) of 2-acetylthiophene[4] was added all at once and the mixture maintained at reflux with stirring for four hours. It was filtered hot through a layer of Hyflo Super-cel and the dioxane and other volatiles stripped under a short column at atmospheric pressure, removing final traces of solvent at water pump vacuum. The residue was fractionated through a 20-cm. Vigreux column at 92-93° (11 mm.) to give 30 g. (43%) of a yellow oil with a rather piercing odor.

The glyoxal gave a violet coloration with concentrated sulfuric acid, rapidly formed a solid derivative with saturated aqueous sodium bisulfite and gave a solid hydrate on warming with twice its volume of water and allowing to stand for two hours. The hydrate was washed with pentane and recrystallized from benzene to give a product melting at 93°[5] (Fujise,[1] 94°). The monosemicarbazone, prepared from the hydrate in the usual manner, melted at 222° (dec.).[5]

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[1] Fujise, *Biochem. Z.*, **236**, 241 (1931).

[2] Kröhnke and Börner, *Ber.*, **69**, 2006 (1936).

[3] Riley and Gray, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., 1943, p. 509.

[4] Supplies through the courtesy of Socony-Vacuum Oil Company.

[5] All melting points were taken with a Fisher-Johns apparatus.

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Traces of Oxygen in Hydrogen or Nitrogen

BY HERMAN A. LIEBHAFSKY AND EARL H. WINSLOW

During the war, oxygen determinations on "oxygen-free" gases were required in the Research Laboratory. A method sensitive to 0.0001% oxygen by volume was developed to