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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HAVANA, CUBA
RECEIVED JULY 22, 1946

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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 Supercel 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.

RESEARCH LABORATORY
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RECEIVED NOVEMBER 12, 1946

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 meet this need,[1] and the results relating to gas purification thereby obtained are given below. All samples for analysis were taken under steady-state conditions.

Experimental

Oxygen Removal by Hot Copper.—In repeated attempts, no oxygen could be detected by this method in hydrogen passed at 110 cc./min. through a fused silica tube (diameter 7 cm., length, 22 cm.) filled with copper turnings at 600°. (The glass purification train, in which all joints were sealed, also contained sodium hydroxide pellets to remove hydrogen sulfide.)

With the copper at 230° and other conditions the same, the purified hydrogen contained 0.0017% oxygen by volume.

Oxygen removal in this way from nitrogen is facilitated by adding hydrogen so that the end product is water, not copper oxides.[2] Oxygen determinations were carried out on nitrogen thus purified in a pilot plant, the copper being near 400°. In one case, 0.0009% oxygen was found in the purified gas, which contained 25% by volume of hydrogen. In a second installation, the oxygen content was 0.0002% at the exit of the purifier with only 3% hydrogen present. Higher purity was not required in the pilot plant, and these oxygen contents probably are not valid lower limits.

Contamination in Transit.—The oxygen content of "oxygen-free" hydrogen being passed through about 10 feet of rubber tubing jumped to 0.0026%. At a distance from the purifier in a steel system believed to be tight, the second nitrogen mentioned above contained 0.0035% oxygen.

These data have been presented in the hope that some one will use the analytical method in a systematic study of oxygen removal, for it is capable of giving quantitative results on gases that could well appear oxygen-free by other quantitative methods.

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(1) Winslow and Liebhafsky, *Ind. Eng. Chem., Anal. Ed.*, **18**, 565 (1946).

(2) So long as the metal is exposed, oxygen removal by copper at red heat can be very effective though repeated contact appears to be necessary for complete removal; *v.* Moser, "Die Reindarstellung von Gasen," Ferdinand Enke, Stuttgart, 1920, p. 79. When, owing to oxide formation, diffusion has become the rate-determining step oxygen removal necessarily suffers. There is no doubt that the addition of hydrogen *facilitates* the process. Hydrogen seems first to have been used for this purpose by Hulett, THIS JOURNAL, **27**, 1415 (1905) who, however, used essentially an oxyhydrogen torch to prepare nitrogen from air.

Though equilibrium favors the formation of ammonia under our experimental conditions, the rate of formation is almost certainly negligible since the homogeneous reaction is too slow and since copper at 400° does not adsorb appreciable nitrogen; *v.*, Frankenburger, *Z. Elektrochem.*, **39**, 276 (1933), and Dew and Taylor, *J. Phys. Chem.*, **31**, 281 (1927).

RESEARCH LABORATORY
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SCHENECTADY, NEW YORK

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The Reaction of Sodium 1-Dodecanesulfinate with Mercuric Chloride[1]

BY C. S. MARVEL, C. E. ADAMS AND RAYNER S. JOHNSON

Reports[2] indicate that German investigators thought their activated Buna-S recipes called Redox formulas were dependent in part on the presence of small amounts of sulfinic acid salts in their emulsifier, Mersolat. In seeking methods of identifying and determining alkylsulfinic acids in the presence of alkylsulfonic acids, we have investigated the reaction of sodium 1-dodecanesulfinate with mercuric chloride. The formation of arylmercury chlorides from arylsulfinates by heating with aqueous mercuric chloride is well known[3] although the analogous reaction of alkylsulfinates has apparently not been reported. We have found that sodium 1-dodecanesulfinate does react readily with mercuric chloride in boiling aqueous solution to give 1-dodecylmercury chloride in 49% yield. Thus, the reaction is demonstrated to be a useful one in the aliphatic sulfinic acid series.

Experimental

Sodium 1-Dodecanesulfinate.—This salt was prepared by the method of Allen.[4] The crude salt showed at least 74% sulfinate content on potentiometric titration in acetic acid with sodium nitrite.[5,6] An anhydrous sample of the salt was also prepared and analyzed both for the elements and for sulfinate content.

Anal.[7] Calcd. for $C_{12}H_{25}SO_2Na$: C, 56.24; H, 9.83; Na, 8.97. Found: C, 56.30; H, 9.99; Na (as Na_2SO_4), 8.88.

The anhydrous material showed over 94% sulfinate by potentiometric titration.[6]

1-Dodecylmercury Chloride.—Using a modification of the procedure of Whitmore, Hamilton and Thurman,[8] 1 g. (0.0037 mole) of pure dry sodium 1-dodecanesulfinate was added with mechanical stirring to a boiling solution of 50 cc. of water and 1 g. (0.0037 mole) of mercuric chloride. A flocculent white precipitate formed immediately and the stirring and heating were continued for two hours. The insoluble product was separated from the reaction mixture by filtration, dried and extracted three times with 20-cc. portions of boiling benzene. Evaporation of the solvent from the filtered benzene extracts gave 0.73 g. (0.0018 mole, 49.3% of the theoretical amount) of crude 1-dodecylmercury chloride, m. p. 106–111°. After crystallization twice from benzene and once from ethanol the product melted at 113–113.5°.

Anal.[7] Calcd. for $C_{12}H_{25}HgCl$: C, 35.55; H, 6.21. Found: C, 35.73; H, 6.51.

Meals[9] has reported the melting point of 1-dodecylmercury chloride as 114–114.5°.

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(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) Swann and Elias, Off. Pub. Bd., U. S. Dept. Commerce, Report PB 1636, 1945.

(3) Connor in Gilman's "Organic Chemistry," 2nd ed., Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 918.

(4) Allen, *J. Org. Chem.*, **7**, 23 (1942).

(5) Koenigs, *Ber.*, **11**, 615 (1878).

(6) We are indebted to Dr. H. A. Laitinen, Mrs. Nancy Fritz and Mrs. Rita Leubner for these titrations.

(7) Microanalyses were done by Mr. H. S. Clark, Illinois State Geological Survey.

(8) Whitmore, Hamilton and Thurman, "Organic Syntheses," 2nd ed., Coll. Vol. 1, John Wiley and Sons, Inc., New York, 1941, p. 519.

(9) Meals, *J. Org. Chem.*, **9**, 211 (1944).

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED SEPTEMBER 3, 1946

Black "Soap" Films of Fatty Acids in Sulfuric Acid

BY LEON MCCULLOCH

Bubble-films of soapy water become thinner on aging, passing through a series of color spectra,