m. p. 219°, $[\alpha]^{25}D$ −28° (18.7 mg. in 2.0 cc. chloroform, $\alpha^{25}D$ −0.26, 1-dm. tube). *Anal.* Calcd. for $C_{35}H_{48}O_6N_2$: C, 70.92; H, 8.16. Calcd. for $C_{36}H_{50}O_6N_2$: C, 71.25; H, 8.30. Found: C, 71.24, 71.15; H, 8.24, 8.28.[6]

Hydrogenation of Brassicasterol.—Brassicasterol (0.13 g.) in ethanol was hydrogenated at atmospheric pressure in the presence of 0.1 g. of palladium black for twenty-four hours. The crystalline residue left on evaporation of the ethanol gave a faint Liebermann color test. Upon recrystallization from ethanol the test was negative. The colorless leaflets contained solvent of crystallization, m. p. 142°, $[\alpha]^{25}D$ +23.6 (22.1 mg. in 2.0 cc. chloroform, $\alpha^{25}D$ +0.26, 1-dm. tube). The carbon values were about 2% low due to unremovable solvent of crystallization.

Brassicastyl Acetate.—The acetate, prepared by refluxing with acetic anhydride for thirty minutes, was recrystallized from ethanol as colorless leaflets, m. p. 143°, $[\alpha]^{25}D$ +14.5° (18.0 mg. in 2.0 cc. chloroform, $\alpha^{25}D$ +0.13, 1-dm. tube). *Anal.* Calcd. for $C_{31}H_{54}O_2$: C, 81.16; H, 11.86. Found: C, 81.12; H, 11.82.

(6) Analyses reported in this paper were carried out by Mr. J. F. Alicino, Fordham University.

Brassicastyl *m*-Dinitrobenzoate.—To a solution of brassicastanol in dry pyridine was added an excess of *m*-dinitrobenzoyl chloride and the solution was heated on the steam-bath for one hour. Water was added, the precipitate filtered, and recrystallized from benzene–ethanol: colorless leaflets, m. p. 202°, $[\alpha]^{25}D$ +13.9° (15.8 mg. in 2.0 cc. benzene, $\alpha^{25}D$ +0.11, 1-dm. tube). *Anal.* Calcd. for $C_{35}H_{52}O_6N_2$: C, 70.43; H, 8.78. Calcd. for $C_{36}H_{54}O_6N_2$: C, 70.79; H, 8.91. Found: C, 71.00, 71.07; H, 8.75, 8.77.

Summary

Brassicasterol has been isolated from unrefined rapeseed oil. The empirical formula $C_{29}H_{48}O$ is more probable than the formula $C_{28}H_{46}O$ given in the literature.

Catalytic hydrogenation of brassicasterol yields a saturated sterol different from its isomer stigmastanol.

NEW BRUNSWICK, N. J. RECEIVED NOVEMBER 23, 1938

[CONTRIBUTION FROM THE UNITED STATES DEPARTMENT OF AGRICULTURE, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE]

Replacement of the Diazo Group by the Acetoxy Group. II. The Preparation of *m*-Bromophenyl and *m*-Iodophenyl Acetates

BY L. E. SMITH AND H. L. HALLER

In the course of a study of the relative toxicity of the isomeric halogenated phenols to goldfish, the results of which will be reported elsewhere, it was necessary to prepare *m*-bromophenol and *m*-iodophenol. The procedures recorded for their preparation were tried,[1,2] but the resulting compounds were difficult to purify and the yields were low.

Recently it has been shown that *m*-chlorophenyldiazonium borofluoride interacts with acetic acid to give *m*-chlorophenyl acetate[3] in good yield. As the acetate can be hydrolyzed readily to the free phenol, the reactions provide a useful method of preparing phenols.

It now has been found that the *m*-bromophenyldiazonium and *m*-iodophenyldiazonium borofluorides also react with acetic acid to give the corresponding acetates, from which the free phenols are obtained on saponification. They have been identified as their phenoxyacetic acid derivatives. No rearrangement of the acetates with the formation of hydroxy methyl ketones has been observed.[4]

(1) Diels and Bunzl, *Ber.*, **38**, 1486 (1905).

(2) Ullmann, *Ann.*, **332**, 38 (1904).

(3) For previous article see Haller and Schaffer, THIS JOURNAL, **55**, 4954 (1933).

(4) Smith and Haller, *ibid.*, **56**, 237 (1934).

Experimental

***m*-Bromophenyldiazonium Borofluoride.**—This compound was obtained in the usual manner by treating a solution of *m*-bromophenyldiazonium chloride with a 40% solution of hydrofluoroboric acid. The yield was 94.5%. The product melted at 145°.[5]

***m*-Bromophenyl Acetate.**—Fifty-one and two-tenths grams of *m*-bromodiazonium borofluoride was heated cautiously with 200 cc. of glacial acetic acid under reflux until the evolution of nitrogen ceased. Then the solution was refluxed for five minutes, concentrated under reduced pressure, and diluted with water. The oil that separated was extracted with ether, and the ether solution was washed with sodium bicarbonate solution and then with water and dried over anhydrous sodium sulfate. The remaining oil was distilled under reduced pressure. It boiled at 95–96°, (2 mm.); yield 19.3 g.

Anal.[6] Calcd. for $C_8H_7BrO_2$: C, 44.65; H, 3.25. Found: C, 43.99, 43.92; H, 3.20, 3.19.

***m*-Bromophenol.**—Nineteen grams of *m*-bromophenyl acetate in 100 cc. of ethyl alcohol and 65 cc. of 10% aqueous potassium hydroxide was refluxed for one hour. The solution was then concentrated under reduced pressure, made acid with dilute sulfuric acid, and extracted with ether. The ether solution was extracted with sodium bicarbonate solution, washed with water, dried over anhy-

(5) All melting points are uncorrected.

(6) Analyses were made by F. Acree, Jr., of the Division of Insecticide Investigations.

drous sodium sulfate, and then concentrated. The yield was 12.7 g. The product was identified as *m*-bromophenol by the preparation of its phenoxyacetic acid derivative.[7] It melted at 110°: mol. wt. (titration), calcd. 231; found 235.

m-**Iodophenyldiazonium Borofluoride.**—This compound was prepared in the usual manner from *m*-iodophenyldiazonium chloride and 40% hydrofluoroboric acid. The yield was 80.5%. It melted at 134°.

m-**Iodophenyl Acetate.**—This compound was prepared from *m*-iodophenyldiazonium borofluoride and acetic acid according to the procedure described for the corresponding bromo compound. It boiled at 132–133° (7 mm.); yield 65.0%.

(7) Koelsch, THIS JOURNAL, **53**, 304 (1931).

Anal. Calcd. for $C_8H_7IO_2$: C, 36.64; H, 2.67. Found: C, 35.91; H, 2.68.

m-**Iodophenol.**—Eleven grams of the acetate, on hydrolysis with 30 cc. of 10% aqueous potassium hydroxide, gave 8.7 g. of the free phenol, which was identified as its phenoxyacetic acid derivative. The melting point was 118°; mol. wt. (titration), calcd. 278; found 273.

Summary

m-Bromophenol and *m*-iodophenol have been prepared by hydrolysis of the acetate obtained by the action of acetic acid on the corresponding diazonium borofluorides.

WASHINGTON, D. C. RECEIVED NOVEMBER 17, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

Certain Derivatives of the Ethers of Hydroxyhydroquinone[1]

BY H. W. DORN, W. H. WARREN AND J. L. BULLOCK

A systematic investigation of the literature for information concerning the derivatives of the ethers of hydroxyhydroquinone revealed that very few had been prepared. Because monosubstitution by halogenation, nitration and sulfonation of the 1,2,4-trimethyl ether yielded only the 5-derivative, the number of mono- and disubstituted compounds possible was limited. But since a means was devised whereby a 3- or 6-monosubstituted hydroxyhydroquinone could be obtained, entirely new series of derivatives were prepared.

Such a synthesis was available from the fact that a hydroxybenzaldehyde in an alkaline medium can be oxidized to a polyphenol by hydrogen peroxide.[2] We were in this way able to transform certain vanillin and isovanillin derivatives into otherwise unattainable hydroxyhydroquinone compounds.

Theoretical

Bromo Derivatives.—Of the three monobromohydroxyhydroquinone trimethyl ethers possible, the 5-compound has been prepared by direct bromination.[3]

The 6-bromotrimethyl ether has not been prepared but Dakin[2] synthesized the 6-bromohydroxyhydroquinone 2-methyl ether by the action of hydrogen peroxide on the potassium salt of 5-bromovanillin. We prepared this compound and then treated it with dimethyl sulfate in the usual manner to obtain the corresponding trimethyl ether.

An attempt was made to prepare the third isomer starting with 2-bromoisovanillin.[4] This was treated with hydrogen peroxide and the product methylated. A small yield of highly colored crystals was obtained which did not give analytical results of sufficient accuracy to indicate the presence of only 3-bromohydroxyhydroquinone trimethyl ether.

Concerning the dibromo bodies, only one of uncertain structure[3] has been prepared. Assuming this to be the 3,5-(rather than 5,6-)dibromohydroxyhydroquinone trimethyl ether, we prepared the 6-bromotrimethyl ether and treated this with bromine in benzene solution. The product was the 3,6-dibromo compound, the 5,6-possibility being eliminated as follows: Dimroth[5] prepared a 2,3(or 5,6)-dibromoquinone but on reduction the compound rearranged to the more stable 3,6-dibromo derivative of hydroquinone. Also, Kohn and Guttmann[6] have shown that when 3,6-dibromo structures are treated with nitric acid, the radicals attached to the phenolic oxygen on the 1,4-carbon atoms are eliminated and a quinone results. We obtained such a quinone from the new dibromotrimethyl ether.

By brominating the 5-bromotrimethyl ether

(1) This paper was constructed from a portion of a dissertation presented by H. W. Dorn to the Department of Chemistry of Clark University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1938.

(2) H. D. Dakin, *Am. Chem. J.*, **42**, 492 (1909).

(3) R. Fabinyi and T. Széki, *Ber.*, **43**, 2681 (1910).

(4) H. Pauly, *ibid.*, **48**, 2018 (1915).

(5) Dimroth, Eber and Weber, *Ann.*, **446**, 132 (1925).

(6) M. Kohn and L. W. Guttmann, *Monatsh.*, **45**, 573 (1924).