Dehydration of 9-Fluorenylcarbinol.—One gram of 9-fluorenylcarbinol in 10 cc. of xylene, refluxed with phosphorus pentoxide for thirty minutes, yielded, after evaporation of the xylene at room temperature, nearly 1 g. of yellow solid. On recrystallizing twice from alcohol it was obtained in colorless plates, m. p. 97°. No change in m. p. resulted when the substance was sublimed in vacuum.

Anal. Calcd. for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.27; H, 5.90.

This product formed a picrate, m. p. 144° (lit., phenanthrene picrate, m. p. 145°).

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CHICAGO, ILLINOIS RECEIVED SEPTEMBER 21, 1940

Oxidation of the Hydroxybiphenyls

BY J. C. COLBERT AND CURTIS LEE HENSLEY

Substitution in *o*- and *m*-hydroxybiphenyl leads to isomers whose orientation must be established. While in one such study[1] in this Laboratory structure was established by a second synthesis of the new compound, this common method is not always available. It has been long known[2] that upon oxidation certain halogenated biphenyls yield benzoic or substituted benzoic acids, thus indicating the position of substituents. Although a systematic study[3] of polyhalogenated biphenyls has been reported, oxidation of the hydroxybiphenyls has been neglected. The formation of benzoic acid by the oxidation of a substituted hydroxybiphenyl would indicate the ring entered by the substituent, while formation of a substituted hydroxybenzoic acid would orient groups entering the ring containing the phenolic group. The present investigation represents a preliminary study of the conditions necessary for the formation of benzoic and hydroxybenzoic acids from the hydroxybiphenyls.

The method of oxidation followed is a modification of the use of chromic anhydride in acetic acid solution.[4] After standardizing the procedure by a study of the oxidation of biphenyl a study was made of the oxidation products from *o*-, *m*- and *p*-hydroxybiphenyl, 3-bromo-4-hydroxybiphenyl, 3,5-dibromo-4-hydroxybiphenyl and 3,5-dinitro-2-hydroxybiphenyl. In all of these cases benzoic acid and a small amount of unchanged starting material were the only substances isolated. Yields were low and differences insufficient to establish influences due to groups and their positions in the ring.

The phenolic ring in the hydroxybiphenyls may be protected against complete oxidation in two ways, namely, by the steric effect of nitro groups in the diortho positions, and by the protective influence of a heavy ester group. 3,5-Dinitro-4-hydroxybiphenyl yields 3,5-dinitro-4-hydroxybenzoic acid, while in the case of 3-nitro-4-hydroxybiphenyl no benzoic acid and only a trace of the corresponding hydroxybenzoic acid could be isolated. When 2-hydroxybiphenyl was converted into the benzenesulfonate[5] and submitted to oxidation the only product isolated was benzenesulfonylsalicylic acid. This ester was readily transformed into salicylic acid.

Procedure

Benzoic Acid from Biphenyl.—Thirty-five grams of chromic anhydride in 32 cc. of 37.5% acetic acid was added drop by drop with vigorous mechanical stirring and occasional warming over a period of thirty minutes to a hot solution of 5 g. of biphenyl in 50 cc. of glacial acetic acid. The reaction mixture was refluxed gently with stirring for two hours. The flame was removed, 6 cc. of acetaldehyde in 15 cc. of glacial acetic acid added, and gentle refluxing continued for an additional fifteen minutes; 50 cc. of water and 50 cc. of saturated salt solution was then added. The reaction mixture was extracted three times with ether, the ether distilled off and the residue made basic with concd. ammonium hydroxide. Solution in alcohol followed by dilution with water led to the recovery of 0.43 g. of unchanged biphenyl. The filtrate from the addition of ammonium hydroxide was acidified with concd. hydrochloric acid, boiled with Norit, filtered and cooled. The product gave 0.26 g. of benzoic acid upon recrystallization from water. An additional 0.20 g. was obtained by ether extraction of the filtrates. A second ether extract of the reaction mixture gave 0.32 g. of benzoic acid. Steam distillation of the reaction mixture (400 cc. of distillate) gave a small amount of impure acid. A second steam distillation, which was concentrated after making it alkaline, gave 0.55 g. of the acid. A final ether extraction of the reaction mixture yielded 0.21 g. more of the acid. The total weight of benzoic acid obtained from 5 g. of biphenyl was 1.54 g. or 38.88%. The addition of concd. hydrochloric acid to the reaction mixture gave a low yield, 5.7% of *m*-chlorobenzoic acid. When the oxidation was repeated with very slight modifications the yields of benzoic acid were as follows: from *o*-, *m*-, and *p*-hydroxybiphenyl 17.2%, 10% and 11.2%, respectively. 3-Bromo-4-hydroxybiphenyl, 3,5-dibromo-4-hydroxybiphenyl and 3,5-dinitro-2-hydroxybiphenyl gave 14.3%, 16.67% and 16.4% of benzoic acid. 3,5-Dinitro-4-hydroxybiphenyl gave a 5.0% yield of 3,5-dinitro-4-hydroxybenzoic acid and upon oxidation the benzene sulfonate of 2-hydroxybiphenyl gave 16.35% yield of benzenesulfonylsalicylic acid. The hydrolytic trans-

(1) Colbert, Meigs and Jenkins, THIS JOURNAL, **59**, 1122 (1937).
(2) Schultz, *Ann.*, **174**, 206 (1874).
(3) Case, THIS JOURNAL, **61**, 3487 (1939).
(4) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Inc., Boston, Mass., 1935, p. 230.
(5) Hazlet, THIS JOURNAL, **59**, 287 (1937).

formation of this substance into salicylic acid was 70% efficient.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OKLAHOMA
NORMAN, OKLAHOMA RECEIVED JUNE 15, 1940

Preparation of Tetramethylene Bromide

BY SHERMAN FRIED AND RICHARD D. KLEENE

Tetramethylene bromide has previously been available by the reaction between N-benzoylpyrrolidine and phosphorus pentabromide.[1] We have now found that the cleavage of tetrahydrofuran by hydrogen bromide, which is analogous to the reaction previously applied by Starr and Hixon,[2] for the preparation of the corresponding chlorohydrin, is much simpler and gives a comparable yield from more readily available starting materials.

Furan was prepared by the decarboxylation of furoic acid in the presence of copper oxide and quinoline,[3] using, however, a Dewar jacketed trap cooled with dry-ice to prevent entrainment of the furan by escaping carbon dioxide. The furan was readily hydrogenated in 95% yield to tetrahydrofuran using palladium–palladium oxide as a catalyst.[4]

Dry hydrogen bromide was passed into the tetrahydrofuran in a flask fitted with a side-tube, reflux condenser and thermometer, until the temperature reached 150°, when the theoretical quantity of hydrogen bromide had been added. The resulting black tarry product was washed thoroughly with water and then with sodium bicarbonate solution until it was free of hydrobromic acid. It was then taken up with ether and dried over anhydrous copper sulfate. The product was fractionated under diminished pressure and 134 g. (yield, 70%) of tetramethylene bromide (b. p. 198° at normal pressure) was collected.

The authors gratefully acknowledge the assistance of Professor W. G. Brown, who designed the apparatus used in the preparation of the furan.

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(2) Starr and Hixon, THIS JOURNAL, **56**, 1595 (1934).
(3) Wagner and Simmons, *J. Chem. Ed.*, **13**, 270 (1936).
(4) Shriner and Adams, THIS JOURNAL, **46**, 1683 (1924).

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS RECEIVED AUGUST 23, 1940

The Isolation of Eriodictyol and Homoeriodictyol. An Improved Procedure

BY T. A. GEISSMAN

The question of the existence of a substance having vitamin-like properties in its effect upon capillary permeability, and called "Vitamin P" by Szent-Györgyi[1] remains unanswered. So far practically all the studies that have been made upon the putative vitamin have been made upon "citrin," a crude flavanone fraction isolated from lemon peel. Reports of experiments in which this material has been used in clinical studies and in animal (guinea pig) tests are conflicting[2] and allow no definite conclusion to be drawn as to the physiological action of "citrin," although the balance of the evidence seems to support the belief that it does contain some substance which exerts a vitamin-like action, when acting in conjunction with vitamin C, in certain types of hemorrhagic diathesis.

Szent-Györgyi has attributed the vitamin activity of "citrin" to the presence of an eriodictyol glycoside[3] although definite experimental proof of its presence in "citrin" is lacking. It is probable, however, that "citrin" does contain eriodictyol (as a glycoside?) since certain color tests (ferric chloride, hot aqueous alkali) shown by "citrin" are also given by pure eriodictyol. It is clear that even if it can be shown that "citrin" contains eriodictyol this will not constitute proof that eriodictyol is "vitamin P." Indeed, Scarborough's results[2c] indicate that hesperidin (also a constituent of "citrin") has "citrin" activity in certain types of purpura.

In an approach to the problem through studies on pure flavanones which are known to be or suspected of being present in "citrin" the preparation of pure eriodictyol has been undertaken.

Eriodictyol (5,7,3′,4′-tetrahydroxyflavanone) has been isolated from *Eriodictyon californicum* by Power and Tutin[4] and from *Lespedeza cyrtobotrya* by Ohira.[5] It has been isolated, along with homoeriodictyol, for the present study from *Eriodictyon californicum* by a procedure which combines the best features of the method of Power and Tutin with those of the method used by Mossler[6] in isolating homoeriodictyol from the same plant. The yields of both eriodictyol and homoeriodictyol were about double those obtained by Power and Tutin but this improvement may not be inherent in the present method since studies now in progress in this Laboratory have indicated that considerable variation can occur

(1) Szent-Györgyi, *et al.*, *Nature*, **138**, 27, 798 (1936); *Z. physiol. Chem.*, **255**, 216 (1938).
(2) (a) Szent-Györgyi, *et al.*, *Nature*, **139**, 326 (1937); **140**, 426 (1938); (b) Zilva, *Biochem. J.*, **31**, 915, 1488 (1937); (c) Scarborough, *ibid.*, **33**, 1400 (1939).
(3) Bruckner and Szent-Györgyi, *Nature*, **138**, 1057 (1936).
(4) Power and Tutin, *Pharm. Rev.*, **24**, 301 (1907); *Pharm. J.*, **77**, 381 (1906); Tutin and Clewer, *J. Chem. Soc.*, **95**, 81 (1909).
(5) T. Ohira, *J. Agr. Chem. Soc. Japan*, **9**, 448 (1933).
(6) Mossler, *Ann.*, **351**, 223 (1907).