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Iodination of Anisole

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Remsen⁴ found that p-hydroxybenzaldehyde and protocatechuic aldehyde, respectively, are not readily oxidized by potassium permanganate solution. Tiemann⁵ could not oxidize vanillin, the 3-methyl ether of protocatechuic aldehyde, into vanillic acid by the usual methods, and Brady and Dunn⁶ failed to oxidize 5-bromovanillin with acetic acid solution of chromic acid and also by alkaline solution of potassium permanganate.

The behavior of many vanillin substitution products⁷ toward the last-named reagent is now being studied. If the hydroxyl group in position 4 is exposed almost all the starting material is recovered. When the alkyl derivatives are used the corresponding acids are obtained. Results thus far indicate that the weight of the alkyl group may determine the yield of product. When a heavy alkyl is present the yield is low.

⁴ Fittig and Remsen, *Ann.*, 159, 150 (1871).

⁵ Tiemann, *Ber.*, 9, 415 (1876).

⁶ Brady and Dunn, *J. Chem. Soc.*, 107, 1859 (1915).

⁷ Raiford and Wells, *J. Am. Chem. Soc.*, 57, 2500 (1935).

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IODINATION OF ANISOLE

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As a rule direct iodinations do not proceed readily, often explained as due to the unfavorable equilibrium attained with the reverse reaction of hydrogen iodide upon the iodo-compound. Iodine is more commonly introduced into an aromatic nucleus through the Sandmeyer reaction by the addition of potassium iodide to a diazotized primary aromatic amine. Thus p-iodoanisole has been prepared from p-anisidine.¹

A procedure of direct iodination for the preparation of iodoaromatic compounds would appear to offer important advantages. In 1901, Brenans² reported such a process in the preparation of p-iodoanisole through the interaction of an absolute ethyl alcohol solution of anisole with mercuric oxide and iodine. Later in 1912, Kauffmann³ used the same procedure for the iodination of resorcinol dimethyl ether to produce 1-iodo-2, 4-dimethoxybenzene, al-

¹ Reverdin, *Ber.* 29, 1000 (1896).

² Brenans, *Bull. Soc. Chim.* [3] 25, 819 (1901).

³ Kauffmann, *Ber.* 45, 2334-35 (1912).

though he made no reference to the earlier work of Brenans. Blicke and Smith⁴ in 1928 modified the Brenans procedure for preparation of p-iodoanisole for which they claimed more desirable results.

As a result of our experience, we have adopted a procedure more nearly like that of Brenans, giving a better yield and product than would appear from his report, and less involved procedure than that of Blicke and Smith. One mol quantity of anisole is dissolved in about four weight quantities of absolute ethanol, three fourths mol quantity of commercial mercuric oxide is added and slightly more than one mol quantity of iodine introduced in five portions with mechanical shaking between portions until the color of iodine nearly vanished. Finally the whole mixture is shaken for about eight hours on a mechanical shaker. The undissolved mercury compounds are filtered, washed with ethanol, the ethanol removed by distillation, the residual oil dissolved in ether and filtered again if necessary, the ether solution washed with a potassium iodide solution, the ether evaporated, the residual oil steam distilled, and the organic part of distillate crystallized from about 85 per cent ethanol. A yield of 85 per cent, melting at 50.5-51.5 (corrected), was obtained.

Some speculation with reference to the role of HgO as a catalyst for this iodination is given.

⁴ Blicke and Smith, J. Am. Chem. Soc. 50, 1229-30 (1928).

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BIOCHEMICAL RECOVERY FROM ANOXIA

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Confinement for 24 hours in pure nitrogen produces a great rise in blood sugar and lactate and fall in blood pH and bicarbonate, and tissue glycogen, in turtles. Recovery follows return to room air. pH and bicarbonate rise to or slightly above normal within 24 hours. Lactate falls markedly in the first 24 hours and is almost down to normal after 2 days; the sugar level falls more slowly but is normal within four days. Glycogen recovery is more rapid