NOTES

The Preparation of *p*-Iodo-anisole.—A convenient method for the preparation of *p*-iodo-anisole has been described by Brenans,[1] through the interaction of an alcoholic solution of anisole with mercuric oxide and iodine. We prepared a considerable quantity of iodo-anisole from the above-mentioned compounds but found it advisable to modify the method in several essential respects. Only one-half of the amount of iodine used by Brenans is necessary; furthermore, carbon tetrachloride is a more suitable solvent than alcohol and an elevated temperature seems to exert a favorable influence on the course of the reaction. A three-necked, round-bottomed, liter flask was fitted with a mechanical stirrer in the following manner. A short piece of rubber tubing was attached to one end of a short glass tube and the other end of the latter was passed through a cork which fitted the large neck of the flask. The stirrer was then inserted into the glass tube, which served as a guide for the shaft of the stirrer, and the rubber tube which fitted the stirrer shaft tightly prevented the escape of liquid around the latter. The two smaller necks of the flask were fitted with an inlet and an outlet tube, respectively. The inlet tube was closed with a calcium chloride bulb and ended about two inches above the surface of the reaction mixture. The outlet tube was attached to a small Drechsel wash bottle, which served as a trap and was cooled with ice. The Drechsel bottle was connected to a suction pump. Forty-three and two-tenths g. of anisole (0.4 mol. equivalent), 200 cc. of dry carbon tetrachloride and 23.2 g. of yellow mercuric oxide (the total amount of mercuric oxide added was 53.2 g. or 0.5 mol. equivalent) were put into the flask and stirred rapidly. Iodine was then added in approximately 10g. portions until 100.8 g. (0.4 mol. equivalent) had been added. The remainder of the mercuric oxide was added in two parts, a 20g. and a 10g. portion during the course of the reaction. During the addition of the iodine the reaction mixture was heated to 50–60° and a fairly rapid stream of air was sucked through the flask. Carbon tetrachloride, iodine and water collected in the trap and at intervals this mixture was removed, dried with calcium chloride and then returned to the reaction flask.

After four hours the reaction mixture was filtered, the inorganic residue thoroughly washed with hot carbon tetrachloride and the carbon tetrachloride filtrate was shaken with sodium bisulfite solution and finally with a small amount of potassium iodide solution in order to remove any unchanged iodine and dissolved mercuric iodide. The carbon tetrachloride layer was dried with fused sodium sulfate and distilled. The portion which boiled below 200° was discarded and the residue in the distilling flask was poured into an evaporating dish and allowed to crys-

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[1] Brenans, *Bull. soc. chim.*, [3] **25**, 819 (1901).

tallize. Any oil present was drained off and the product was then recrystallized from 25 cc. of alcohol, filtered and washed with a small amount of the same solvent. The average yield of pure material was 69 g. or 73% of the calculated amount; m. p. 49–52°. In order to determine whether or not the product was contaminated with the higher boiling di-iodo-anisole, 110 g. of the purified iodo-anisole was distilled. The product boiled at 139–139.5° and not more than a gram of residue remained in the distillation flask.

When the reaction was carried out at ordinary temperature the average yield of *p*-iodo-anisole from two experiments was 57%.

Iodine is rapidly decolorized by mercuric oxide in the presence of water. In one instance a mixture of iodine, mercuric oxide and water was stirred until the iodine was completely decolorized. Anisole was then added and the mixture was stirred again for eight hours. No iodo-anisole was produced. It is obvious that the removal of water formed during the preparation of iodo-anisole is desirable. When the water given in the reaction was not removed by a stream of air we found that in addition to mercuric iodide a colorless, inorganic compound was formed. This substance liberated iodine from acidified potassium iodide solution and was, no doubt, mercuric iodate resulting from decomposition of the unstable mercuric hypo-iodite, one of the initial products of the interaction of iodine, mercuric oxide and water.

We found that iodine did not react with anisole if mercuric oxide was replaced by lead oxide or calcium oxide. If the mercuric oxide merely serves to destroy the equilibrium

$$CH_3OC_6H_5 + I_2 \rightleftharpoons CH_3OC_6H_4I + HI$$

as is ordinarily supposed, it seems strange that lead oxide and calcium oxide should be inactive.

Although anisole can be mercurated quite readily[2] and the following series of reactions can be carried out during the course of four to five hours, this method for the preparation of *p*-iodo-anisole is impractical since the final reaction product consists of a mixture of anisole, *o*- and *p*-iodo-anisole and di-iodo-anisole.

$$CH_3OC_6H_5 + Hg(OCOCH_3)_2 = CH_3OC_6H_4{-}HgOCOCH_3 + CH_3COOH$$
$$CH_3OC_6H_4{-}HgOCOCH_3 + NaCl = CH_3OC_6H_4HgCl + CH_3COONa$$
$$CH_3OC_6H_4HgCl + I_2 = CH_3OC_6H_4{-}I + HgICl$$

The above process does not gain in practicability even though it is possible to separate the *p*-anisylmercuric chloride from its ortho isomer since this operation involves considerable time and labor.

Iodine chloride reacts vigorously with anisole but there seems to be formed a complex mixture of iodo and chloro substitution products of anisole.

[2] Dimroth, *Ber.*, **35**, 2867 (1902).

By the interaction of potassium iodide with diazotized *p*-anisidine a 75–80% yield of pure *p*-iodo-anisole can be obtained.

Contribution from the
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Received January 19, 1928
Published April 5, 1928

Note on the Purification of Brucine.[1]—Brucine has come to be the alkaloid most commonly used in resolving optically active acids. The free base can be recovered after the resolution and used over and over. If one tries to obtain the alkaloid by precipitating it with ammonium hydroxide from a solution of the hydrochloride, the result is a paste which is difficult to filter and impossible to wash adequately.

The following procedure gives a crystalline product of a high degree of purity. To the solution of brucine hydrochloride is added about one-fifth its volume of ethyl alcohol. The solution is then made definitely alkaline with ammonium hydroxide. After standing for several hours crystals begin to appear. Sometimes twenty-four to forty-eight hours or even longer must elapse before crystallization starts. In about a week the precipitation is complete. The crystals are filtered, washed and air-dried. They are then ready for use again in resolution.

Contribution from the
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Received February 3, 1928
Published April 5, 1928

A Variation of the Carius Method for the Determination of Sulfur.—Among the various modifications of the Carius method for the determination of sulfur, it is frequently suggested that bromine[1] or a few crystals of potassium bromide[2] be added to the fuming nitric acid. This modification probably arose through the observation that halogenated compounds are more readily oxidized.[3] Rupp[4] introduced the variation of placing a barium salt in the tube with a marked shortening of the time required to gather the resulting sulfate. He was aware of Carius' observation as to the greater ease of oxidation of chlorine containing compounds but did not correlate the use of barium chloride with any observed

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[1] This work has been conducted under a grant from the Douglas Smith Foundation for Medical Research of the University of Chicago.

[1] Angeli, *Gazz. chim. ital.*, **21**, [1] 163 (1891).

[2] Thorpe and Whiteley, "Students Manual of Organic Chemical Analysis," Longmans, Green and Co., London, **1926**, p. 59.

[3] Carius, *Ann.*, **116**, 19 (1860).

[4] Rupp, *Chem.-Ztg.*, **32**, 984 (1908).