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-

---

[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.

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

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
COLLEGE OF PHARMACY OF THE
UNIVERSITY OF MICHIGAN
F. F. BLICKE
F. D. SMITH

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
PHYSIOLOGICAL CHEMISTRY LABORATORY OF THE
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS
FELIX SAUNDERS

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

---

[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).

increase in the ease or extent of oxidation. The fact that chlorine is a better halogenating agent than bromine led the authors to carry out the following series of comparative experiments on the oxidation of sulfonal by means of modifications of the Carius method.

One-tenth gram of sulfonal was oxidized by means of 3 cc. of fuming nitric acid (sp. gr. 1.60) with the addition of the substances noted below. A temperature of 200° was chosen to allow for an oxidation slow enough for comparison.

TABLE I

RESULTS OF SULFUR ANALYSES

Per cent. of Theoretical Sulfur Appearing as Sulfate

Time of heating, hrs.	I HNO_3	II HNO_3 and Br_2	III HNO_3 and $BaBr_2$	IV HNO_3 and $Ba(NO_3)_2$	V HNO_3 and $BaCl_2$	VI HNO_3 and $NaCl$
6	14.2	6.6	22.8	20.1	50.7	32.1
12	25.2	23.4	41.1	44.0	75.6	75.6
24	46.2	49.6	57.8	66.4	84.4	95.6
48	70.6	71.7	72.1	85.6	95.2	99.5

In series II four drops of bromine was used in each. In series V 0.1915 g. of barium chloride (enough to give 5% excess) was used. In III, IV and VI the salts shown were used in quantities equivalent to the barium chloride in V.

It appears from the table above that Rupp's modification is more thorough in its oxidation than either nitric acid alone or nitric acid and bromine. The use of sodium chloride also markedly increases the ease of oxidation.

Although Rupp's method has been checked[5] and extended to microanalysis,[6] the authors have found that too frequently the opening of the Carius tube is accompanied by chips of glass falling into the tube's contents, from which they cannot be removed. For the oxidation of those sulfur compounds which give rise to stable sulfones, the authors suggest the introduction of 0.3 to 0.4 g. of sodium or potassium chloride and 3 cc. of fuming nitric acid with the sample to be analyzed. After heating, cooling and opening, the contents of the tube, together with the washings, can be filtered and evaporated to dryness, providing sufficient sodium chloride has been used to fix the sulfate formed. The analysis can then be continued in the regular manner.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

RECEIVED FEBRUARY 16, 1928
PUBLISHED APRIL 5, 1928

VICTOR C. ROGERS
GREGG DOUGHERTY

---

[5] Schneider, *Ber.*, **42**, 3417 (1909).

[6] Pregl-Fyleman, "Quantitative Organic Microanalysis," Blakiston's Son and Co., Philadelphia, **1924**, p. 126.

Chlorine Dioxide Explosion.—It seems proper to issue a warning as to possible danger in the oxidation of primary alcohols by means of chlorate and dilute sulfuric acid in presence of vanadium pentoxide as described by Milas.[1]

A first trial of this interesting reaction, as applied to *n*-butyl alcohol, was uneventful, but gave a smaller yield than was expected, and a second trial was undertaken. This had proceeded about thirty minutes beyond the addition of the specified 18 cc. of 6 *N* sulfuric acid (see p. 498) when a detonation of the utmost violence occurred in the reflux condenser, scattering a shower of glass with great force. The reaction flask was undisturbed by the detonation.

It must be stated that Milas' directions were in both experiments modified by use of potassium instead of sodium chlorate, and that in the second trial the quantities of 5% sulfuric acid and chlorate were increased about 10% in the hope of decreasing the amount of alcohol unattacked; after the explosion part of the chlorate was still present in solid form. At the time of the accident the liquid was boiling gently.

Communication with Dr. Milas reveals the fact that, except in the oxidation of methyl alcohol (for which a special and safer procedure is described), sixty-two trials of the method were made with no explosion. He also states the substitution of potassium for sodium chlorate to be inadmissible, the former being "much more reactive" and also more likely to cause explosion because of its lower solubility in water. Most important, there is pointed out the absolute necessity for regulating the temperature of the liquid to 75–80° during and also following any addition of fresh acid. This appears clearly stated in the general directions (p. 495), but in the specific directions the first period of heating to 75–80° is followed by a period of *boiling*, and then more acid is introduced and the "heating" is continued. Throughout the directions the word "heating" is used, in a sometimes puzzling sequence, to imply either a temperature of 75–80° or the boiling temperature of the mixture.

In the interest of safety, therefore, it seems wise to emphasize the apparently urgent need for such a control of temperature that the liquid is not above 80° when fresh acid is added, and that this temperature be not exceeded until some time after the final addition of acid has been made.

According to Dr. Milas the method is quite safe if the conditions are properly controlled. It is hoped by this emphasis upon the conditions whose control is important, the oxidation may be rendered as free from hazard as is claimed. A very vivid recollection of a storm of glass, and the fact that the ill-fated experiment, heated only about five and a

---

[1] Milas, This Journal, **50**, 493 (1928).

half hours, gave a very fair yield of ester, have combined to satisfy the writer's curiosity.

HARRISON LABORATORY
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PENNSYLVANIA

E. C. WAGNER

RECEIVED MARCH 24, 1928
PUBLISHED APRIL 5, 1928

NEW BOOKS

Oxidation-Reduction Reactions in Inorganic Chemistry. By ERIC R. JETTE, Ph.D., Assistant Professor of Chemistry, Washington Square College, New York University. The Century Company, 353 Fourth Avenue, New York, 1927. xvi + 152 pp. 10 figs. 13 × 19.5 cm. Price $1.10.

The author has discussed oxidation-reduction equations from two viewpoints: the "valence-change" and the "ion-electron" methods. The principles behind this book have been developing gradually since the publication of Ostwald's "Grundlinien der Anorganischen Chemie" about thirty years ago and have been taught from the electronic point of view in certain technical schools and colleges even before Alexander Smith in his "General Chemistry for Colleges" in 1914 brought out a scheme for balancing such equations. In recently published modern textbooks more than fifty per cent. of the equations discussed and studied are of the oxidation-reduction type. The author has attempted to explain these changes and methods of balancing equations for the student who has not had physical chemistry, the qualitative rather than the quantitative side being emphasized.

Topics discussed are: oxidation-reduction in relation to atomic structure; balancing equations of non-ionic type (valence change type) and those in aqueous solutions (ion-electron type); cell reactions and activity of metals; effect of hydrogen-ion concentration applied to manganese and nitrogen reactions; application of the ion-electron method to insoluble and weakly dissociated compounds, and the formation of complex ions in reactions in which oxidation-reduction changes take place. The book contains four appendices: the thermodynamic basis of the ion-electron method; in tabular form all common oxidizers and reducers, the main products of their oxidation-reduction action and notes on conditions of their reaction; oxidation-reduction potentials; a table of ionization constants of weak inorganic acids. References to the literature are given at the ends of chapters.

The book will appeal to students who wish to round out their cultural chemistry course, to advanced students in inorganic chemistry and to students of qualitative analysis. All teachers interested in modern ways of presenting inorganic chemical facts will be interested in reading this book.

EDWARD MUELLER