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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**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.

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**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 micro-analysis,[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.

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

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