

micro scale by titration with potassium bromate-bromide solution. Best results were obtained by modifying the original procedure of Francis and Hill as follows. Approximately 0.05 g. of the resorcinol was dissolved in 10 ml. of glacial acetic acid in a 250-ml. Erlenmeyer flask. An excess (35-45 ml.) of a solution 0.021 molar in potassium bromate and 0.11 molar in potassium bromide was added and the mixture cooled in an ice-bath and acidified with 5 ml. of 50% sulfuric acid. After five minutes sufficient glacial acetic acid was added to dissolve the precipitate, the

flask removed from the ice-bath, 1 ml. of a saturated potassium iodide solution was added and the iodine titrated in the usual way. The bromate-bromide solution was standardized against pure orcinol. The tribromo-alkylresorcinols were isolated and their melting points determined.

In Table V are summarized the data for the 5-*n*-alkyl-resorcinols, results of the previous investigators already mentioned being enclosed in brackets.

Summary

1. 3,5-Dimethoxybenzamide reacts with *n*-alkylmagnesium bromides to give high yields of the corresponding ketones. These are useful intermediates for the preparation of the 5-*n*-alkyl-resorcinols.

2. 5-*n*-Butyl- and 5-*n*-hexylresorcinol have been described for the first time.

3. The bactericidal properties of the 5-*n*-alkylresorcinols have been reported.

4. An improved procedure for the bromate-bromide titration of resorcinol derivatives has been developed.

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TABLE V

5-*n*-ALKYLRESORCINOLS

Alkyl	Yield, %	B. p., °C.	M. p., Mm.	Hydrate	M. p., °C. Anhyd.	M. p., °C. tribromo compd.
<i>n</i> -Propyl	80	148-149	3	47	86.5-87	97.5-98
		[169]	8]	[42-51]	[82-84]	[99]
<i>n</i> -Butyl ^a	66	151-152	3	81.5-82.5 ^c	84-84.5
<i>n</i> -Amyl	72	162-164	5	[40-41]	85
		[164	5]			[87]
<i>n</i> -Hexyl ^b	65	192-195	11	49-49.5 ^d	75-76
<i>n</i> -Heptyl	60	179-181	6	55-55.5	73.5-74.5
				[57]		[75]

^a Anal. Calcd. for 0.1043 g. of C₁₆H₁₄O₂: 32.60 ml. KBrO₃ soln. Found: 32.56 ml. ^b Anal. Calcd. for 0.0835 g. of C₁₂H₁₀O₂·H₂O: 20.44 ml. KBrO₃ soln. Found: 20.52 ml. ^c Fine needles from toluene. ^d After three crystallizations from water.

[CONTRIBUTION FROM THE JESSE METCALF CHEMICAL LABORATORY AT BROWN UNIVERSITY]

The Extraction of Germanium and Gallium from Germanite. III. The Recovery of Germanium from the Arsenious Sulfide Sublimates

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In the process developed in this Laboratory for the removal of germanium and gallium from germanite, the finely ground ore is first heated in a stream of dry, oxygen-free nitrogen at 800°¹ to remove all of the arsenic. At the same time a small amount of the germanium, present as germanic sulfide, is volatilized. The partially sintered residue subsequently is heated at 825° in a reducing atmosphere (ammonia) whereupon the germanic sulfide present in the ore is converted to the more volatile germanous sulfide which sublimes to the cooler regions of the apparatus where it collects in the form of very pure crystals. The gallium is recovered by means of a hydrochloric acid extraction of the non-volatile residue.

The loss in weight of the ore in the first operation is about 13.5%, and 75% of the loss is accounted for in a highly colored, yellow-orange, sublimate which is collected in an iron condenser. Analyses of many lots of the sublimate

(1) Johnson, Foster and Kraus, *THIS JOURNAL*, **57**, 1828 (1935); Foster, Johnson and Kraus, *ibid.*, **57**, 1832 (1935).

have shown it to be chiefly arsenious sulfide, containing varying quantities of germanium, occasionally as much as 4%, present as germanic sulfide, GeS₂. In the particular sample referred to, this quantity of germanium amounted to 8.6% of the total germanium in the ore.

From the treatment of more than 100 kg. of germanite, about 10 kg. of these germanium bearing arsenic sulfide sublimates had been collected. In the most commonly used method of recovering the germanium, the material is oxidized with concentrated nitric acid, the product dissolved in hydrochloric acid, and distilled in a stream of chlorine, whereupon germanium tetrachloride is collected in the receiver. For a complete separation from arsenic, a second distillation is usually necessary.²

With large quantities of material, the method outlined is very laborious, and a method was sought in which the complete oxidation of the

(2) See, however, Aitkenhead and Middleton, *Ind. Eng. Chem., Anal. Ed.*, **10**, 633 (1938), published after this work was completed.

arsenious sulfide sublimates could be eliminated. The most promising separation appeared to be that developed by Abrahams and Müller,³ who showed that arsenic is precipitated quantitatively as arsenious sulfide from a slightly acid solution, with the removal of none of the germanium. Upon increasing the acidity to 6 normal or greater, the germanium can be precipitated quantitatively as germanic sulfide. Evidently germanium sulfide is hydrolyzed in solutions of lower acidity and not precipitated. Preliminary work⁴ with 200-g. samples of the arsenic sulfide residues showed that it was feasible to dissolve the mixed arsenic and germanium sulfides in strong ammonia solution and effect the separation after neutralizing the extract. The following procedure was adopted.

The material was sifted through a 20-mesh screen to remove the fused lumps. (The part which did not pass the screen was crushed in an iron mortar and carried separately through the same extraction procedure.) Seven hundred gram lots of the sifted material were each stirred mechanically into a liter of strong (12 normal) ammonium hydroxide contained in a 4-liter wide-mouthed bottle. Stirring was continued for a few hours and the mixture allowed to stand for two days. The extract was filtered through a large Büchner funnel and the residue returned to the bottle for a second extraction with another liter of ammonium hydroxide. The residue (20%) left after the second filtration was washed with distilled water. Analysis of samples of the residual material, carried out by means of the germanium tetrachloride distillation method, showed that the germanium removal was adequately complete. Less than 2% of the original germanium remained unextracted.

The filtrate and washings were neutralized, separately, with 6 normal sulfuric acid and brought finally to a pH between 2 and 1. At this stage the volume of the solution was about 6 liters. Arsenic sulfide precipitated copiously as neutralization proceeded, but not completely. The thick suspension was transferred to a 12-liter bottle, and saturated with hydrogen sulfide under slight pressure. The bottle was agitated on a large mechanical shaker. After being shaken for two or three hours, the solution usually was saturated, but occasionally it was found necessary to readjust the pH to effect complete removal of the arsenic. The precipitate, after filtration, was washed with a total quantity of 4 liters of 0.1 normal sulfuric acid, this large volume of wash solution being required before tests on the filtrate showed only traces of residual germanium.

To check the completeness of separation, with some lots

(3) Abrahams and Müller, *THIS JOURNAL*, **54**, 86 (1932).

(4) Unpublished observations of Ralph G. Schaubhut in this Laboratory, 1933.

the entire arsenious sulfide precipitate was dissolved in ammonium hydroxide and reprecipitated. The observations of Abrahams and Müller, that the separation is nearly quantitative, were confirmed.

Attempts were made to concentrate the germanium in the wash solution by precipitating magnesium germanate⁵ but in the presence of hydrogen sulfide this procedure failed.

The 6 liters of filtrate and the 4 liters of wash solution were acidified, separately, to an acid concentration of 6 normal, by the addition of the requisite volume of approximately 18 normal sulfuric acid (prepared by adding a liter of concd. sulfuric acid to 1.1 liter of water, and cooling to room temperature).

As the acid was added most of the germanium was precipitated as pure white germanic sulfide but, to ensure complete precipitation, the suspension was saturated with hydrogen sulfide under slight pressure, and agitated as described above. The voluminous precipitate was allowed to settle and the supernatant liquid removed through a "filter stick."⁶ Filtration was completed using a Büchner funnel and the precipitate was washed with 6 normal sulfuric acid. The filtrates and wash liquors were tested with hydrogen sulfide for germanium and resaturated when more than a trace was present.

To convert the product to germanium oxide, the bulky germanium sulfide precipitates were oxidized by means of concentrated nitric acid. The oxide produced was heated finally to about 800°. The very pure germanium dioxide produced is soft, friable and readily removed from the crucible.

The quantities involved in the handling of 10 kg. of sublimates were approximately the following:

6280 g. sublimates, 20 mesh, of which 5014 g. dissolved.
3925 g. ground lump, of which 2535 g. dissolved.

Volume of neutralized extract, 14 gallons, with 5 gallons of wash liquor.

Volume of filtrates, arsenic free, acidified to 6 *N*, 35 gallons.

Volume of 6 *N* wash acid, about 20 gallons.

Quantity of germanium dioxide recovered, 340 g.

Summary

The arsenious sulfide sublimates, obtained as a by-product of the sublimation process of separating germanium from germanite ore, contain sufficient germanium to warrant recovery. The arsenic and germanium in an ammoniacal extract of the sublimates are separated by fractional precipitation of the respective sulfides by controlling the hydrogen ion concentration. Pure white germanic sulfide is produced.

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(5) Müller, *THIS JOURNAL*, **44**, 2496 (1922).

(6) Morton, "Laboratory Technic in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, p. 167.