separated. The benzene layer was washed three times with 50-cc. portions of 10% hydrochloric acid and this followed by three washings with 50-cc. portions of 10% sodium hydroxide and a final washing with water. The various aqueous layers were washed successively with a 50-cc. portion of benzene and this was added to the main benzene solution. In the first four runs plotted in Curve I, Fig. 1, where a considerable excess of benzoyl chloride remained at the end of the reaction, it was necessary to modify the method of purifying the benzene solution. It was found that even hot dilute sodium hydroxide would remove the benzoyl chloride only very slowly. This difficulty was overcome by treating the benzene solution, after washing with hydrochloric acid, with 75 cc. of an aqueous alcoholic solution of sodium hydroxide prepared by adding an equal volume of 95% alcohol to a 12*N* solution of sodium hydroxide. It is essential that a decided excess of sodium hydroxide be present to prevent the formation of ethyl benzoate.

The purified benzene solution was dried over calcium chloride, the benzene distilled, and the residual oil heated *in vacuo* to 160° (thermometer in liquid) at 25-mm. pressure. The resulting crude benzophenone was weighed for yield.[8] The results are plotted in Figs. 1 and 2.

Summary

1. The yield of benzophenone prepared by the reaction of benzoyl chloride with benzene in the presence of mixtures of ferric chloride and aluminum chloride, has been found to be approximately the mean of that obtained using pure ferric chloride and pure aluminum chloride.

2. The ferric chloride has a detrimental action which is apparently due to the acceleration or inauguration of an unknown side reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ALBERTA]

THE MERCURATION OF BETA-RESORCYLIC ACID

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During the course of a study of the mercuration of resorcinol and some resorcinol derivatives,[1] it was decided to mercurate a carboxylic acid derivative of resorcinol. β-Resorcylic acid was selected for this work, because of the three carboxylic acid derivatives of resorcinol it is probably the easiest to prepare.

It has been found that β-resorcylic acid very readily forms monomercurated and dimercurated derivatives. The compounds produced are somewhat similar in properties to the corresponding mercurated alkyl resorcinols.[1] The reactions involved are also similar. The β-resorcylic acid derivatives, however, seem to form more stable compounds. For instance, they do not darken appreciably when exposed to sunlight. Also they are

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[8] The yields were more readily duplicated using this procedure than by calculating the yield on the distilled product. On distillation practically the entire amount came over between 184 and 186° at 25 mm.

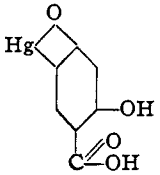
[1] Sandin, THIS JOURNAL, 51, 479 (1929).

more soluble in alkali solutions and these solutions are more stable than the alkali solutions of the mercurated alkyl resorcinols.

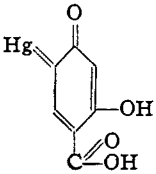
Very recently Fox and Whitmore[2] have found that certain organic compounds can be mercurated in alkaline solution, while other compounds of similar structure cannot. In this work it has been found that β-resorcylic acid is readily mercurated in alkaline solution.

The authors have noticed, as was also the case in the previous work on resorcinol compounds, that a yellow to brown color is associated with the mercurated derivatives which presumably have an anhydro structure. For that reason it is suggested that an alternative structure which involves a quinoid grouping might be used. (Compare formulas I and II. There is no evidence in this work that the substance corresponding to formula II may not be of a para quinoid form instead of the ortho.)

I



II



The mercurated derivatives described cannot be purified by crystallization. They readily lose acetate groups and form anhydro groups, especially on the application of heat. For these reasons, in order to prepare compounds of definite and constant mercury content, the experimental conditions must be constant and rigidly followed. The starting materials must also be quite pure.

Experimental Part

Anhydro-5-hydroxymercuri-β-resorcylic Acid.—The β-resorcylic acid used in this preparation and in subsequent work was obtained from the Eastman Kodak Co. Some β-resorcylic acid was also prepared for this work by the action of potassium bicarbonate on resorcinol.[3] Three and eight-tenths g. (0.02 mole).[4] of β-resorcylic acid dissolved in about 25 cc. of hot glacial acetic acid was added to a hot solution of 3.18 g. (0.01 mole) of mercuric acetate in 25 cc. of glacial acetic acid. The resulting solution was heated for a few minutes and then poured into about one liter of cold water. It was allowed to stand for twelve hours. The white solid (probably the monohydroxymercuri-β-resorcylic acid) was filtered off, washed with water and then dried in the air oven at 100° for twelve to twenty-four hours. It became slightly colored. There was probably the loss of water to form the anhydro-5-hydroxymercuri-β-resorcylic acid. The yield was 95% It is soluble in a solution of sodium hydroxide.

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[2] Fox and Whitmore, This Journal, 51, 2196 (1929).

[3] Nierenstein and Clibbens, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1930, Vol. X, p. 94.

[4] The above quantity and also the calculation of the percentage yields of mercurated derivatives are based upon the assumption that the β-resorcylic acid is anhydrous.

Anal. Calcd. for $C_7H_4O_4Hg$: Hg, 56.9; acetic acid, 0. Found: Hg, 56.8, 56.7, 57.1, 56.3; acetic acid, 0.[5]

The probable structure of this compound is indicated by formula I or II.

In order to prove the position of the mercury group, one molecular proportion of iodine was added to a suspension of one molecular proportion of the monomercurated compound in glacial acetic acid. This mixture was allowed to stand for about twelve hours, with occasional warming and stirring. The filtrate from this mixture was diluted with water, the precipitate filtered off and extracted with alcoholic alkali. The mono-iodo acid was recovered from the extract by dilution with water and acidification. The product melted at 172° without further purification. Nicolet and Sampey[6] give 172° as the melting point of 5-iodo-2,4-dihydroxybenzoic acid.

Anhydro-3-hydroxymercuri-5-acetoxymercuri-β-resorcylic Acid.—Three and eight-tenths g. (0.02 mole) of β-resorcylic acid dissolved in 50 cc. of hot alcohol was added to a boiling solution of 12.72 g. (0.04 mole) of mercuric acetate in 300 cc. of alcohol and 5 cc. of glacial acetic acid. Almost instantly a pale yellow solid separated. It was immediately filtered off by suction and washed with hot alcohol. It was air-dried for three days. The yield was 11.6 g. or 95%. It is soluble in a solution of sodium hydroxide, but otherwise insoluble in the ordinary organic solvents.

Anal. Calcd. for $C_9H_6O_6Hg_2$: Hg, 65.6; acetic acid, 9.8. Found: Hg, 64.8, 64.8; acetic acid, 9.1. Other preparations of this compound gave the following percentages for mercury: 66.4, 66.1, 65.6, 65.5.

Of the several attempts to replace the mercury groups by iodine, according to the procedure outlined above, only one was apparently successful. The di-iodo acid obtained decomposed at 191–195°.

Nicolet and Sampey[6] give the decomposition range of 3,5-di-iodo-2,4-dihydroxybenzoic acid as 193–196°.

In the preparation of the above dimercurated derivative, if a large amount of glacial acetic acid was used and practically no alcohol, or if the experiment as already described was carried out and then followed by a heating on the water-bath, a precipitate which was white and not yellow was obtained. This compound was probably the di-acetoxymercuri-β-resorcylic acid. However, attempts to obtain it pure by using glacial acetic acid as the medium were unsuccessful. The material on drying gradually lost acetic acid and became colored. The mercury content at the same time gradually approached that required for the anhydro-3-hydroxymercuri-5-acetoxymercuri-β-resorcylic acid.

Mercuration of β-Resorcylic Acid in Alkaline Solution.—β-Resorcylic acid was converted into a dimercurated derivative, in alkaline solution according to the procedure of Fox and Whitmore.[2] The mercurated compound was precipitated by bubbling carbon dioxide through the alkaline solution or by nearly neutralizing the solution with dilute hydrochloric acid. The compound, which was brown in color, was probably anhydro-3,5-dihydroxymercuri-β-resorcylic acid. The yield was 80%.

Anal. Calcd. for $C_7H_4O_5Hg_2$: Hg, 70.4. Found: Hg, 69.9, 69.4, 69.3, 71.4.

Summary

1. The mercuration of β-resorcylic acid gives mono and dimercurated products.

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[5] It was evident that the carbon dioxide formed by the decomposition of the β-resorcylic acid [Hemmelmayr and Meyer, *Monatsh.*, **46**, 143 (1916)] would interfere with the titration of acetic acid by the regular method [White, This Journal, **42**, 2355 (1920)]. For this reason a blank determination was carried out on β-resorcylic acid and phosphoric acid, making conditions as similar to the actual determinations as possible.

[6] Nicolet and Sampey, This Journal, **49**, 1796 (1927).

2. The anhydro compounds obtained are colored in such a way as to indicate the possibility of quinoid structure.
3. β-Resorcylic acid can be mercurated in alkaline solution to give a dimercurated product.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

THE THERMAL DECOMPOSITION OF GASEOUS GERMANIUM TETRAETHYL

BY RAY L. GEDDES[1] AND EDWARD MACK, JR.

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In connection with the modern theory of the mechanism of gaseous reactions it probably would be very helpful to study the kinetics of decomposition of a series of molecules which present a stepwise gradation of structure and stability. With this in mind we have begun an investigation of the thermal decompositions of the tetra-alkyls (such as the tetramethyls and tetraethyls) of carbon, silicon, germanium, tin and lead. This family of compounds presents a considerable variety of sizes of the central atom, a great difference of bonding forces with which the outlying groups are bound to the central atom, and affords the possibility of examining related molecules of various degrees of complexity. Preliminary study shows that the temperatures of appreciable decomposition extend over a wide range, from about 220° for lead tetraethyl to about 650° for silicon tetramethyl, and that in at least two cases, germanium tetraethyl and lead tetraethyl, and probably in all of the other cases, the decomposition is predominantly homogeneous and unimolecular. The present paper is an account of the behavior of germanium tetraethyl. Data for the other compounds will be presented in later papers.

The thermal decomposition of gaseous germanium tetraethyl in the range 420–450° is a reaction about 98% homogeneous, and unimolecular down to pressures of about 8 cm. During the course of the decomposition, metallic germanium is deposited as a semi-mirror, or as what amounts to a sputtered film, on the walls of the reaction vessel, and it seems natural to represent the primary reaction as

$$Ge(C_2H_5)_4 \longrightarrow Ge + 4C_2H_5$$

(It must be admitted that this is only a suggested manner of decomposition, and that there is not enough evidence to justify setting up a detailed reaction mechanism. A similar formation of free methyl[2] groups seems to be well established in the decomposition of lead tetramethyl.) The free ethyl groups might then be supposed virtually to unite to form normal bu-

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[1] University Fellow, 1929–1930, The Ohio State University.

[2] Paneth and Hofeditz, *Ber.*, 62, 1335 (1929).