[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

A COMPARISON OF PHENYLHYDRAZINE OXALATE WITH MESOXALIC ACID PHENYLHYDRAZONE.

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While making an examination of the products obtained by the oxidation of potassium lactate by means of potassium permanganate in the presence of small quantities of potassium hydroxide, Paul A. Davis and one of us found a white, leafy, mother-of-pearl, crystalline mass after acidifying the filtrate from the oxide of manganese with acetic acid and then adding a solution of phenylhydrazine in diluted acetic acid.[1] This substance was associated with the pyruvic acid phenylhydrazone from which it could be easily separated, owing to the fact that it was difficultly soluble in alcohol. This compound was found to be identical in every respect with the compound described by Causse as mesoxalic acid phenylhydrazone, m. p. 163° to 164°.[2] Causse obtained this compound from bismuth mesoxalate which he had prepared by the oxidation of glycerol by means of a mixture of bismuth nitrate, potassium nitrate and nitric acid. On the other hand, Fischer[3] describes mesoxalic acid phenylhydrazone as a substance which crystallizes from hot water or dilute alcohol in fine yellow needles. According to Elbers[4] it has the following composition: $C_6H_5.NH.N = C(COOH)_2$, and melts between 163° and 164°. Clemm[5] gives the melting point of this compound as 174° if heated quickly. A comparison of the compound obtained by Fischer and that obtained by the repetition of Causse's experiments, showed that they were two entirely different substances. A careful examination of the compound obtained by Causse proved that it was phenylhydrazine oxalate, $(C_6H_5.NH.NH_2)_2(COOH)_2$, identical with the salt described by Fischer as that compound.[6]

An analysis of the compound gave the following results: Carbon, 54.74%, 54.80%; hydrogen, 6.03%, 5.69%; theory, carbon, 54.87%; hydrogen, 5.92%. The percentage composition of mesoxalic acid phenylhydrazone is as follows: Carbon, 51.92%; hydrogen, 3.85%.

Preparation of Phenylhydrazine Oxalate.—Fischer[7] prepared phenylhydrazine oxalate by mixing ether solutions of phenylhydrazine and oxalic acid. The following method for preparing this compound was found to give the salt in a better physical condition. A solution of 8.57 g.

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[1] A similar observation was made by Mr. Paul Cottringer of this laboratory while studying propylene glycol under similar conditions.

[2] *Bull. soc. chim.*, [3] **11**, 696 (1894); Beilstein, "Org. Chem.," **1**, 394, *Ergz.*

[3] *Ber.*, **16**, 2241 (1883); **17**, 578 (1884).

[4] *Ann.*, **227**, 335 (1885).

[5] *Ber.*, **31**, 1451 (1898).

[6] *Ann.*, **190**, 85 (1878).

[7] *Loc. cit.*

(2 mols) of phenylhydrazine in 40 cc. of ethyl alcohol was added to a solution of 5 g. (1 mol) of crystalline oxalic acid dissolved in 125 cc. of the same solvent. The dense, heavy, white precipitate which at once formed was filtered by suction and washed twice with small amounts of ethyl alcohol. After washing with ether, the compound was air-dried. The final product was glistening white with a very slight cream tinge. The yield was 10.94 g., theory, 12.14 g., therefore, 90.15% yield.

Estimation of Oxalic Acid in Phenylhydrazine Oxalate.—The following experiment illustrates a very rapid and accurate method which was developed for the estimation of oxalic acid in phenylhydrazine oxalate. A portion of the salt (1.0020 g.) was suspended in a mixture of 10 cc. of water, 25 cc. of calcium acetate solution (1 cc. = 0.05 g.), 4 cc. of ammonium hydroxide. The reaction mixture was heated to boiling, until all the phenylhydrazine oxalate was converted to calcium oxalate. The oxalic acid was determined either by titration with potassium permanganate, or the calcium oxalate was weighed as calcium sulfate. The following results show the accuracy of this method:

	Oxalic acid.		
G. used.	Found.	Theory.	Method.
1.0020	0.2937	0.2944	Titration
1.0018	0.2937	0.2944	Titration
1.0010	0.2930	0.2941	Gravimetric
1.0178	0.3032	0.2991	Gravimetric
1.0034	0.2939	0.2952	Gravimetric

Preparation of Basic Bismuth Mesoxalate.—An attempt was next made to prepare bismuth mesoxalate and compare its behavior towards hydrogen sulfide with that of the bismuth compound obtained by Causse in the oxidation of glycerol towards the same reagent. The general method employed by Vanino[1] for the preparation of the normal bismuth oxalate was followed. The work of Vanino was repeated and his results were confirmed by analysis. A solution of 38 g. of bismuth nitrate crystals and 14.5 g. of mannitol in 200 cc. of water was prepared as described by Vanino. A solution containing twice the equivalent of mesoxalic acid for making the normal salt was prepared by adding 24 g. of sulfuric acid to 64.4 g. of barium mesoxalate, boiling for a few minutes and filtering. The unused sulfuric acid was removed from the filtrate by the addition to it of 3 g. more of the barium mesoxalate and the above operation was repeated. The final solution measured 300 cc.

The bismuth-mannitol solution was added with constant stirring to the cold solution of mesoxalic acid. The resulting white precipitate appeared to be crystalline but did not settle rapidly. An examination of the filtrate showed that the bismuth had been completely precipitated.

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[1] *Ber.*, 41, 3997 (1908); *J. prackt. Chem.*, 74, 144 (1906).

After filtration the residue was washed with absolute alcohol and absolute ether, and then air-dried. An analysis showed that it was probably a mixture of the normal and the basic salts. The white precipitate was now boiled for some time with the original filtrates, filtered, washed with alcohol and ether, and then air-dried. An analysis of material dried at 100° gave the following results:

Bi_2O_3, 68.99%, 68.88%. The amount of water in the air-dried sample was found to be 9.05% and 9.14%. These results are in fair agreement for those corresponding to the basic salt $Bi(OH)(C_3O_5).2H_2O$, *i. e.*, Bi_2O_3, 68.04%; H_2O, 9.55%.

The compound loses its water of hydration very slowly over sulfuric acid. When dried at 100°, the loss is complete in about three hours. It is easily soluble in concentrated nitric, sulfuric and hydrochloric acids. It is slowly soluble in these acids when they are dilute and cold. This same compound was also prepared by using smaller quantities of materials.

Action of Hydrogen Sulfide on Basic Bismuth Mesoxalate and Normal Bismuth Oxalate.—An experimental study was now made of the action of hydrogen sulfide on the above-prepared basic bismuth mesoxalate, the normal bismuth oxalate described by Vanino[1] and the bismuth compound described by Causse. Five grams each of these compounds were suspended in 250 cc. of water to which had been added 0.65 g. of potassium acid carbonate. Hydrogen sulfide was introduced and the contents of the flasks were frequently shaken as described by Causse until as much as possible of the bismuth had been converted to the sulfide. After filtration, the hydrogen sulfide was removed by boiling under diminished pressure. A solution of 5 g. of phenylhydrazine dissolved in 50% acetic acid was added to each of the above filtrates after they had been previously acidified with acetic acid. The precipitates which were obtained in each case were filtered, washed with a little alcohol and ether, and then dried on a clay plate.

The precipitate obtained from the normal bismuth oxalate of Vanino proved to be phenylhydrazine oxalate identical in every respect with the synthetic product described above. The yield was 2.2 g. The compound obtained from the bismuth mesoxalate of Causse was phenylhydrazine oxalate, being the same as the one obtained from the normal bismuth oxalate. The phenylhydrazine oxalate obtained from the Causse compound was analyzed for its oxalic acid content by the method developed above with the following results:

$C_2H_2O_4$, by titration, 29.12%; by the gravimetric method, 29.29%; theory, 29.41%.

An examination of the melting points of this specimen and that of mesoxalic acid phenylhydrazone showed that they were entirely different substances. From these results one is led inevitably to the conclusion that the bismuth compound obtained by Causse must have been an oxalate.

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[1] *Loc. cit.*

It is of interest in this connection that the analysis obtained by Causse for his compound was as follows: Bi_2O_3, 68.13%; carbon, 10.41%; while the percentage composition of the normal bismuth oxalate is: Bi_2O_3, 68.23%; carbon, 10.59%. The theoretical composition of the above basic bismuth mesoxalate is as follows: Bi_2O_3, 68.04%; carbon, 10.56%.

The precipitate obtained from the basic bismuth mesoxalate was a yellow crystalline compound, identical with mesoxalic acid phenylhydrazone which had been prepared from barium mesoxalate. The yield was 1.95 g. This compound corresponded in every way with that described by Fischer and Elbers.[1] Furthermore, it was found that it did not reduce Fehling's solution in the cold nor did it show the melting-point phenomena described by Behrend and Schulz[2] for the phenylhydrazine salt of mesoxalic acid phenylhydrazone. This latter salt easily reduces Fehling's solution in the cold. It was furthermore found that the melting point of our mesoxalic acid phenylhydrazone was not changed when the compound was crystallized from hot aqueous solutions containing hydrochloric acid. By this latter treatment Behrend and Schulz[2] succeeded in preparing mesoxalic acid phenylhydrazone from the phenylhydrazine salt mesoxalic acid phenylhydrazone.

The silver mesoxalate described by Causse was also prepared and treated with hydrogen sulfide as described above for the several bismuth compounds. The filtrate from the silver sulfide was found to contain oxalic acid as was shown through the formation of phenylhydrazine oxalate. No trace of mesoxalic acid phenylhydrazone was found.

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THE IDENTIFICATION OF ACIDS. III.[3]

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In recent articles[4] it has been shown that *p*-nitrobenzyl bromide is a useful reagent for the identification of acids and some fifty crystalline *p*-nitrobenzyl esters have been described. This investigation has been continued and *p*-nitrobenzyl esters of a number of other acids have been prepared. The object has been to put on record the properties of esters from all available acids so that they may be of service to chemists wishing to identify any of these acids. Several esters are included, the composition of which may be open to question and some have been abandoned which merit further study. So long as a crystalline compound is obtained

[1] *Loc. cit.*

[2] *Ann.*, **365**, 29 (1909).

[3] From the doctor's dissertation of Edward Lyons.

[4] THIS JOURNAL, **39**, 124, 701 (1917).