CLX.—*The Estimation of Phosphorus in Organic Compounds.*

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IN a previous paper (Davies, Pearse, and Jones, J., 1929, 1262) attention was drawn to the difficulty experienced in obtaining satisfactory results in estimations of phosphorus in tertiary alkylphosphines. Low results for phosphate were obtained whether the phosphine was oxidised by fuming nitric acid in a sealed tube, by concentrated nitric and sulphuric acids, or by potassium persulphate and concentrated sulphuric acid, although Poggi and Polverini (*Atti R. Accad. Lincei*, 1926, **4**, 315) found the last method satisfactory in the case of triphenylphosphine. Further work has confirmed our previous conclusion that the oxidation of alkylphosphines by " perhydrol " and sulphuric acid is incomplete on the macroscale.

Collie and Reynolds (J., 1915, **107**, 367) stated that triethylphosphine oxide is unaffected by boiling with any oxidising agent, and is incompletely oxidised by heating in a sealed tube with nitric acid, and similarly Davies and Jones (J., 1929, 33) found tri-*n*-butylphosphine oxide to be very resistant to further oxidation. Since such oxides are probably the primary oxidation products (compare Davies and Jones, *loc. cit.*), their abnormal stability would account for the low analytical results.

(In the analysis of aliphatic sulphides, the stability of the sulphones towards fuming nitric acid causes similar difficulties.)

A second possible cause of the low values for phosphorus obtained with the tertiary phosphines is the difficulty of estimating phosphoric acid in the presence of large quantities of various oxidising agents.

No difficulty, however, has been experienced in estimating by the usual methods the phosphorus content of compounds in which phosphorus is linked through oxygen to carbon, as in the esters of phosphorous and orthophosphoric acids, or where less than three organic radicals are united through carbon to phosphorus and the remaining linkages of the phosphorus atom are to oxygen, as in the phosphonic acids.

To avoid these difficulties a method is here described which requires only a micro-quantity of the phosphine, and is adapted from methods used hitherto only for biological products (compare Baumann, *J. Biol. Chem.*, 1924, **59**, 667; Bell and Doisy, *ibid.*, 1920, **44**, 55; Briggs, *ibid.*, 1922, **53**, 13; 1924, **59**, 255; Eggleton and Eggleton, *Biochem. J.*, 1927, **21**, 190; *J. Physiol.*, 1929, **68**, 193). The phosphine is decomposed by heating with concentrated sulphuric acid, and the oxidation completed by the use of "perhydrol." The phosphoric acid produced is estimated colorimetrically with ammonium molybdate and quinol, comparison being made against a known amount of potassium dihydrogen phosphate. The colorimetric determination depends upon the quantitative reduction of the phosphomolybdic acid to the blue acid, $22MoO_3,2MoO_2,P_2O_5,H_2O$ (Wu, *J. Biol. Chem.*, 1920, **43**, 216).

The method has been successfully applied to the analysis of tertiary phosphines and other pure organic compounds of phosphorus, and has been found to possess very distinct advantages over methods hitherto recommended for that purpose. An estimation can be completed in 2 hours, with an average error of less than 2%, and no tedious precipitations and filtrations are involved.

EXPERIMENTAL.

The following standard reagents are required : (*a*) Sulphuric acid : 15 c.c. of concentrated acid (*d* 1·82) diluted to 100 c.c. with water. (*b*) 5% Ammonium molybdate solution. (*c*) Reducing agent : 0·25 g. of quinol and 7·5 g. of crystallised sodium sulphite dissolved in water and made up to 50 c.c. (*d*) Potassium dihydrogen phosphate solution (1 c.c. = $7·968 \times 10^{-5}$ g. of phosphorus) : 0·0350 g. of the salt diluted to 100 c.c. with water.

Compounds containing Labile Phosphorus.—Where the compound on treatment with water yields orthophosphoric acid, a quantity containing about 0·008 g. of phosphorus is dissolved in water and made up to 100 c.c. 1 C.c. of this solution is transferred by an Ostwald pipette into a measuring cylinder, and about 9 c.c. of water, 2 c.c. of the standard sulphuric acid, and 2 c.c. of the ammonium molybdate reagent are added. The mixture is allowed to stand for 1 hour. The comparison solution is made by diluting 1 c.c. of the potassium dihydrogen phosphate solution to slightly less than 10 c.c. in a measuring cylinder, and adding the same amounts of sulphuric acid and ammonium molybdate as before. 1 C.c. portions of the reducing agent are added simultaneously to the test solution and to the comparison solution, the volumes quickly adjusted to 15 c.c., and after ½ hour the two solutions are compared colorimetrically—a Klett top-reader colorimeter with 60 mm. scale was used.

Determinations on 0·0410 g. of urea phosphate dissolved to 100 c.c. gave P, 19·4, 19·5 (Calc.: 19·6%).

Tertiary Phosphines.—Attempts to determine the phosphorus by treating these compounds with fuming nitric acid in a Carius tube gave only traces of phosphoric acid after 8 hours' heating at 250°; some crystalline solid, soluble in water, appeared on the walls of the tube, and was probably the phosphine oxide.

Preliminary experiments with the new method were carried out by diluting a weighed quantity of phosphine with *ether* to a known volume, and carrying through the process with an aliquot part (1 c.c. containing about 0·08 mg. of phosphorus). The following results were obtained:

	P, % (Found).	P, % (Calc.).
Tri-*n*-butylphosphine	15·1	15·3
Phenyldi-*n*-amylphosphine	12·6	12·4
p-Ethylphenyldi-*n*-propylphosphine	13·6	13·9

The following is the general method to be employed for the estimation of phosphorus in the tertiary phosphines.

A quantity of the phosphine containing about 0·008 g. of phosphorus is weighed into a small glass tube, which is then lowered into a graduated flask. *Redistilled alcohol* is added, and the volume adjusted to 100 c.c., allowance being made for the volume of the glass weighing tube. For the estimation, 1 c.c. of the phosphine solution is heated in a 20-cm. Pyrex boiling tube with 2·5 c.c. * of the reagent sulphuric acid until charring sets in. It is allowed to cool, 3 or 4 drops of " perhydrol " are added, and it is again heated. Oxidation is completed by a further treatment with 2 drops of " perhydrol." In order to destroy any excess of " perhydrol " (or persulphate, which may have been formed) the mixture is evaporated to about 0·5 c.c. twice with 2-c.c. portions of water. The appearance of a yellow colour on the subsequent addition of ammonium molybdate indicates incomplete removal of " perhydrol." The contents of the tube are transferred to a measuring cylinder with about 11 c.c. of water, 2 c.c. of ammonium molybdate and 1 c.c. of the reducing reagent are added, and the volume is adjusted to 15 c.c. After ½ hour, the solution is compared colorimetrically with the comparison solution prepared as described above.

In order to avoid bumping and spurting in the heating, it is essential to keep the boiling tube vigorously rotated by hand in the

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* This quantity is greater than that (2·0 c.c.) used in the comparison solution owing to the necessity for compensating for the loss during the subsequent boiling of the test solution; these quantities ensure that the acidity of each solution is approximately the same during the development of the colour.

flame of the micro-burner, and to hold it at an angle of about 45° from the vertical.

The results tabulated below include trialkyl-, phenyldialkyl-, and *p*-tolyldialkyl-phosphines.

Phosphine.	Amount, g., dissolved to 100 c.c.	P, %.	
		Found.	Calc.
Tri-*n*-propyl-	0·0520	15·0	15·3
Tri-*n*-heptyl-	0·0854	9·6	9·4
Phenyldi-*n*-propyl-	0·0508	15·7	16·0
Phenyldi-*n*-butyl-	0·0588	13·4, 13·6	13·9
Phenyldi-*n*-amyl-	0·0647	12·3, 12·1	12·4
Phenyldi*iso*amyl-	0·0648	12·3	12·4
p-Tolyldi-*n*-butyl-	0·0609	12·8	13·1

Mr. I. K. Jackson, of these Laboratories, has used the authors' method of estimating phosphorus in a number of different types of arylalkylphosphine prepared by him :

Phosphine.	Amount, g., dissolved to 100 c.c.	P, %.	
		Found.	Calc.
p-Xylyldiethyl-	0·0503	16·1, 16·0	16·0
p-Xylyldi-*n*-propyl-	0·0573	13·6, 13·6	13·9
p-Xylyldi-*n*-butyl-	0·0660	12·3, 12·1	12·4
p-Xylyldi*iso*butyl-	0·0659	12·0	12·4
p-Xylyldi-*n*-amyl-	0·0720	10·7, 10·7	11·1
Anisyldi-*n*-propyl-	0·0609	13·6	13·8
Anisyldi-*n*-amyl-	0·0727	11·2	11·1
p-Ethylphenyldi-*n*-butyl-	0·0682	11·9	12·4

Phosphonic Acids.—The usual methods offer no difficulty in the estimation of phosphorus in these acids : *e.g.*, phenylphosphonic acid was fused with a mixture of sodium and potassium carbonates in a nickel basin, the mass extracted with dilute nitric acid, and the phosphoric acid determined by precipitation with ammonium molybdate and weighing as $(NH_4)_3PO_4,12MoO_3$ (Found : P, 19·4, 19·5. Calc. : P, 19·6%).

Although our method can be applied on the micro-scale to these acids (1 c.c. of a solution containing about 8 mg. of phosphorus per 100 c.c.), yet in this case, unlike that of the phosphines (see p. 1209), we are not restricted to small quantities, and oxidation can be effected on a macro-scale. In this way, 0·0412 g. of phenylphosphonic acid was treated with 5 c.c. of concentrated sulphuric acid, warmed, and about 2 c.c. of " perhydrol " were added in small quantities, until oxidation was complete. The mixture was diluted to 100 c.c., and the phosphoric acid in 1 c.c. of this solution determined by colorimetric comparison (Found : P, 19·4. Calc. : P, 19·6%. On the micro-method, P, 19·3%, was found).

*Tri-*n*-butyl Phosphite.*—Low results were obtained in determinations of the phosphorus content of tri-*n*-butyl phosphite when a micro-quantity was boiled with sulphuric acid and subsequently treated with " perhydrol " in a Pyrex boiling tube. This failure was due to volatilisation of the phosphite during the boiling with dilute sulphuric acid in the open tube. The oxidation was, therefore, carried out in a Carius tube by heating the phosphite (0·0610 g.) with 15 drops of fuming nitric acid for 5 hours at 250°. The contents of the tube were washed into a beaker, and the nitric acid removed by evaporation. The residue was diluted to 100 c.c., and 1 c.c. taken for colorimetric comparison (Found : P, 12·7. Calc. : P, 12·4%).

Esters of Orthophosphoric Acid.—Phosphorus may be determined in these esters by the ordinary methods; *e.g.*, by oxidation with a mixture of concentrated nitric and sulphuric acids, neutralisation with ammonia and precipitation with ammonium molybdate, tri-*n*-butyl phosphate (Found : P, 11·9. Calc. for $C_{12}H_{27}O_4P$: P , 11·7%) and tri-*n*-amyl phosphate (Found : P, 10·0. Calc. for $C_{15}H_{33}O_4P$: P, 10·1%) were analysed.

Colorimetric Method with Triphenyl Phosphate.—The phosphorus content of triphenyl phosphate (0·0841 g.) was determined as in the macro-method for phosphonic acids (Found : P, 9·5. Calc. : P, 9·5%).

We wish to thank Dr. McCowan and Dr. Quastel, of the Cardiff City Mental Hospital, for granting us facilities for the preliminary experiments.

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[*Received, March* 17*th,* 1931.]