Summary

1. A new method of synthesis of phenylethylmalonic methyl ester, an intermediate in the production of pheno-barbital, is described.

2. The yields at all stages of the process are good and the method is the most satisfactory of all those known at present.

3. The isolation of the salt, α-sodium-α-phenylbutyric methyl ester, an intermediate product in this synthesis, is discussed. The behavior of the salt indicates that it exists in tautomeric forms, of structures $[(C_6H_5)(C_2H_5)C{=}C(OCH_3)O^-]Na^+$ and $[(C_6H_5)(C_2H_5)C^-(CO_2CH_3)]Na^+$.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

A NEW MICRO PHOSPHORUS DETERMINATION

BY ADALBERT ELEK

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Various methods for the micro determination of phosphorus in organic substances have been described. In most cases, however, the methods used lack either simplicity or accuracy.

The procedure as described by Lieb,[1] though accurate, is inconvenient inasmuch as it involves washing the combustion tube and boiling the boat in dilute nitric acid. The method described by Lieb and Wintersteiner[2] and by Josephson and Sjörberg[3] was found to yield low results for at least one substance, namely, for thymus nucleic acid.

The new method described in this paper eliminates the undesirable features of the methods cited.

Experimental Part

A sample of 3–6 mg. is weighed by difference into a silver crucible of approximately 18 mm. lower diameter, 33 mm. upper diameter and 40 mm. in height. About 0.2 g. of potassium nitrate and 1 g. of potassium hydroxide are then added and the mixture is fused by heating the upper part of the crucible over a small flame with a slow, rotating motion to prevent spattering. In the course of about two to three minutes the fusion is complete, as shown by the clearness of the melt. The crucible is covered and allowed to cool on a copper block. The cooling requires about four minutes. A slight pressure on the walls of the crucible loosens the cake, which is then easily transferred into a large Pyrex test-tube of about 30 mm. diameter and 200 mm. in length. The crucible is then washed 2–3 times with a small quantity of water and the washings are transferred to the test-tube. Enough nitric acid (prepared according to Lieb)[1] is then added to make the volume up to 15 cc. The solution is placed in a boiling water-bath for about ten to fifteen minutes. In some cases the solution is slightly turbid, but on warming in

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[1] Pregl, "Die quantitative organische Mikroanalyse," 2nd ed., Springer (Berlin), **1923**, p. 151.

[2] Lieb and Wintersteiner, *Mikrochemie*, **2**, 78 (1924).

[3] Josephson and Sjörberg, *Svensk Kemisk Tidskrift*, **36**, 267 (1924).

the water-bath the turbidity disappears. Fifteen cc. of molybdate solution (prepared according to Lieb)[1] is then added. The mixture is stirred for about thirty seconds, allowed to stand for a few minutes and then stirred again for a few seconds. The test-tube is covered and allowed to stand for two hours at most, after which time all of the precipitate collects in compact form at the bottom of the test-tube.

The filtration, washing, drying and weighing are carried out as described by Lieb.[1]

Some of the results obtained with pure compounds by this method are given below (Table I).

TABLE I

RESULTS WITH PURE COMPOUNDS

	Subs., mg.	Ammonium phosphomolybdate, mg.	P, calcd., %	P, found, %
Uridine phosphoric acid	3.920	26.345	9.58	9.76
Cytidine phosphoric acid	3.102	20.390	9.61	9.54
Guanylic acid + $2H_2O$	2.960	15.845	7.76	7.77
Adenylic acid + H_2O	4.820	28.265	8.49	8.51
Thymus nucleic acid (Sample I)	2.943	17.490	8.67	8.63
Thymus nucleic acid (Sample II)	3.616	21.329	8.67	8.56

Summary

A new micro method for the determination of phosphorus is described. The analysis is carried out with 3–6 mg. of substance. Data are given for the analysis of some nucleic acid derivatives.

NEW YORK CITY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE IDENTIFICATION OF ORGANOMAGNESIUM HALIDES BY CRYSTALLINE DERIVATIVES PREPARED FROM α-NAPHTHYL ISOCYANATE

BY HENRY GILMAN AND MARGARET FURRY

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Introduction

Organomagnesium halides and other reactive organometallic compounds may be conveniently detected, qualitatively, by the sensitive color test described by Gilman and Schulze.[1] Frequently, however, a need is felt for some reagent that will give a solid derivative characteristic of a given RMgX compound. One of the best compounds for this purpose is phenyl isocyanate, because of its smooth reaction at low temperatures to give anilides. This reaction was first investigated by Blaise,[2] and was later[3]

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[1] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925); also, *Bull. soc. chim.*, **41**, 1479 (1927).

[2] Blaise, *Compt. rend.*, **132**, 38 (1901). Also, Gilman and Kinney, THIS JOURNAL, **46**, 493 (1924), for the mechanism of reaction. Others have used phenyl isocyanate in studies on organomagnesium halides. Recently, Johnson and McEwen, THIS JOURNAL, **48**, 474 (1926), used it for the identification of phenylacetenylmagnesium bromide.

[3] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).