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.

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

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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]

[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).

tried as one of several methods for the quantitative estimation of Grignard reagents. It has been used in connection with the identification of the —NMgX,[4] and —OMgX[5] and —SMgX[6] groups, and for the preparation of derivatives from organocalcium iodides,[7] organobarium iodides,[8] organoberyllium halides[9] and beryllium dialkyls.[10]

α-Naphthyl isocyanate is generally available and enjoys some advantages over phenyl isocyanate for the identification of various organometallic compounds. Its greater molecular weight gives amides that are generally less soluble, better crystallized and higher melting than the corresponding anilides obtained when phenyl isocyanate is used. Furthermore, should an excess of α-naphthyl isocyanate be used, which might often be the case when a derivative is prepared from a very small quantity of organometallic compound, the *sym.*-di-α-naphthyl urea (formed subsequent to hydrolysis) is so sparingly soluble in the commoner solvents, particularly petroleum ether, that the separation and purification of the α-naphthalide are made easier than would be the case if phenyl isocyanate were used. α-Naphthyl isocyanate has recently been used for the identification of beryllium dimethyl.[10] Phenyl isocyanate may be preferred to α-naphthyl isocyanate in some cases where the organometallic compounds are not very reactive.[7,8,9] Phenylcarbamine chloride ($C_6H_5NHCOCl$) and phenylcarbamine bromide are more reactive than phenyl isocyanate,[5] from which compound they may very conveniently be prepared.

The present study reports a number of α-naphthalides prepared from typical Grignard reagents. The reaction is very probably applicable to all RMgX compounds, and inasmuch as it is possible to bring so many halides, alkyl and aryl, into reaction with magnesium, the formation of amides should lend itself to the identification of such halides and the compounds from which the halides are prepared. Marvel, Gauerke and Hill[11] have reported on the use of the Grignard reagent for the identification of primary alkyl bromides and iodides by conversion to the corresponding mercuric halides and Hill[12] has just extended this method to the identification of secondary alkyl and aryl bromides and iodides.

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[4] Gilman and Pickens, THIS JOURNAL, **47**, 2406 (1925).

[5] Gilman and Schulze, *Rec. trav. chim.*, **47** (1928). This paper describes a wide variety of reagents used in studies concerned with the characterization of the —OMgX group. The same reagents can, of course, be used for the identification of organometallic compounds where the metal is attached to carbon.

[6] Gilman and King, THIS JOURNAL, **47**, 1136 (1925).

[7] Gilman and Schulze, *ibid.*, **48**, 2463 (1926).

[8] Gilman and Schulze, *Bull. soc. chim.*, **41**, 1333 (1927).

[9] Gilman and Schulze, THIS JOURNAL, **49**, 2904 (1927).

[10] Gilman and Schulze, *J. Chem. Soc.*, **131**, 2663 (1927).

[11] Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925).

[12] Hill, *ibid.*, **50**, 167 (1928).

Experimental

When an ethereal solution of α-naphthyl isocyanate is added to the Grignard reagent in ether, a smooth reaction takes place and is completed with the addition of the isocyanate. The ethereal solution obtained subsequent to hydrolysis contains the naphthalide. Frequently some *sym.*-di-α-naphthyl urea can be separated by filtration of the solid present at the ether–water interface. The α-naphthalides were purified by crystallization from ethyl alcohol. The process of purification can be considerably simplified by using an excess of Grignard reagent, for in this way, providing proper precautions have been taken to exclude moisture, there should be no formation of the sparingly soluble *sym.*-di-α-naphthyl urea. It has been found possible to prepare very quickly in this way benz-α-naphthalide from one cc. of a 0.05 *N* solution of phenylmagnesium bromide.

The α-naphthalides were identified in each case by a mixed melting point determination with the amide prepared from α-naphthylamine and the appropriate acid chloride.

TABLE I

DATA ON NAPHTHALIDES

RX used in preparation of RMgX	α-Naphthalide	M. p.,[a] °C.
Methyl iodide	Acet-	160
Ethyl bromide	Propion-	126
n-Propyl bromide	*n*-Butyro-	121
n-Butyl bromide	*n*-Valero-	112
Cyclohexyl bromide	Hexahydrobenz-[b]	188
Benzyl chloride	Phenylacet-[b]	166
β-Bromostyrene	Cinnamyl-[b]	217
Bromobenzene	Benz-	161
p-Bromotoluene	*p*-Tolu-[b]	173
α-Bromonaphthalene	α-Naphtho-[b]	236

[a] The melting points recorded here are uncorrected.

[b] No reference to this α-naphthalide was found in the literature.

Summary

Reactive organometallic compounds may be conveniently identified by the formation of α-naphthalides from α-naphthyl isocyanate.

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