

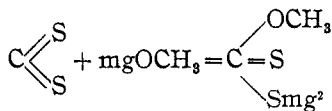
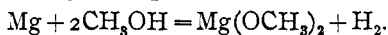
## NOTE.

*A New Synthesis of Ethyl Methyl Xanthic Ester.*—The fact has been pointed out that metallic magnesium and methyl alcohol do not react under the ordinary conditions of temperature and pressure, but upon the addition of a small particle of iodine, or a few drops of a nitro-compound, reaction begins, hydrogen is evolved and the methylate of magnesium is formed.<sup>1</sup> Certain alkyl halides and even carbon bisulphide induce the reaction between magnesium and methyl alcohol.

It is the reaction between carbon bisulphide, methyl alcohol and magnesium that is now to be considered. While making preliminary tests a marked difference in the appearance of the reaction-product was noticed according as magnesium was allowed to react with a dilute or a concentrated solution of carbon bisulphide in methyl alcohol. In the case of the dilute solution the reaction-product was light yellow in color and very thickly gelatinous, this latter property being due to the supposed formation of magnesium methylate. On the other hand, where carbon disulphide was present in excess, no precipitate was formed and the solution was of a deep blood-red color.

These observations led to the conclusion that when magnesium reacts with a solution of carbon bisulphide in methyl alcohol, magnesium methylate tends to form, and this then in turn, in the presence of an excess of carbon bisulphide, reacts to form magnesium methyl xanthate.

These reactions may be represented as follows:

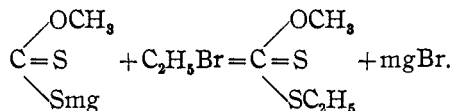


funnel. Again, the outlet opening of the separatory funnel should not be more than 2 or 3 mm. in diameter to prevent the stem from emptying when the stop-cock is turned off. Also, the form and size of the outlet tube at the bottom of the calcium chloride jar should pretty closely approximate the drawing to assist the used acid in running off without filling the tube until it reaches the perpendicular part. The importance of this point is not so apparent until one has experimented with it.

<sup>1</sup> H. S. Fry: This Journal, "Action of Magnesium upon Methyl Alcohol" (yet to be published).

<sup>2</sup> mg =  $\frac{1}{2}$  Mg.

Now if magnesium methyl xanthate is thus formed it should in turn react with an alkyl halide, such as ethyl bromide, to form an ester of the hypothetical methyl xanthic acid, namely, ethyl methyl xanthic ester, in accordance with the following reaction:



That such reactions do actually take place with the final production of ethyl methyl xanthic ester is evident from the following experimental part.

*Experimental Part.*—One-half of a gram-molecule (12 grams) of magnesium, 152 grams of carbon bisulphide (twice the theoretical amount in order to insure an excess), and 500 cc. of methyl alcohol were placed in a 2-liter round-bottomed flask equipped with a long reflux condenser. The reaction began immediately and proceeded with increasing energy so that in the course of about ten minutes the contents of the flask were boiling violently. Five minutes later all of the magnesium had disappeared, and the resulting reaction mixture, which was of a clear deep red-brown color was heated to boiling upon the water-bath for two hours in order to effect complete reaction between the carbon bisulphide and any magnesium methylate that was in solution.

After the contents of the flask had cooled down to the room temperature, 120 grams of ethyl bromide were added. This amount was a slight excess over that actually required to combine with the magnesium as methyl xanthate. As soon as the ethyl bromide was added the contents of the flask became warmer, and in the course of a few minutes were boiling actively. The color of the solution rapidly changed from deep red brown to pale yellow. The reaction mixture was again boiled for two hours to insure complete reaction between the ethyl bromide and the magnesium methyl xanthate.

In order to obtain the ethyl methyl xanthic ester thus formed, a liter of water slightly acidified with sulphuric acid was added to the reaction mixture in the flask. A heavy yellow oil separated out and was extracted with ether in a separatory funnel. The ether solution thus obtained, after being neutralized, washed with water and filtered, was subjected to distillation.

By distillation at boiling-water-bath temperature the ester was freed from ether, carbon bisulphide, ethyl bromide, and methyl alcohol. Further distillation with a direct flame yielded 85 grams of a light yellow oil, distilling at  $184^{\circ}$  C., the boiling-point of ethyl methyl xanthic ester. The yield was 62.50 per cent. of the theoretical.

Further distillation to  $200^{\circ}$  C. resulted in the decomposition of the residue in the distilling flask, a very small quantity of distillate passing over.

This synthesis affords an example of the analogy between magnesium and sodium or potassium methylates which later are commonly used in the preparation of various xanthic esters in accordance with analogous reactions.

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### NEW BOOKS.

URIC ACID. THE CHEMISTRY, PHYSIOLOGY AND PATHOLOGY OF URIC ACID AND THE PHYSIOLOGICALLY IMPORTANT PURIN BODIES WITH A DISCUSSION OF METABOLISM IN GOUT. By FRANCIS H. MCCRUDDEN. New York: Paul B. Hoeber. 1905. 318 pages. Paper: \$2.50; Canvas, \$3.00 net.

In the main this work is a compilation of the important scientific literature on the subject of uric acid in the several relations indicated by the title; these relations are discussed in separate sections and the various sub-topics are so chosen as to practically cover the whole field.

In the preface the author explains the motives which led him to make this extensive compilation. He refers especially to the views held by Haig on the great importance of uric acid in bringing about certain pathological conditions, which views were everywhere treated with a degree of consideration entirely out of proportion to the value of the experiments and observations on which they were based. Few subjects have received more attention from medical writers than has uric acid as a factor in the causation of disease, and the advertising columns of the medical journals and the daily press shown that advantage has been taken of this by enterprising manufacturers in turning out a host of remedies, mostly frauds, for the treatment of the so-called "uric acid diathesis." In no field of medicine is there greater humbug.