lyzed, and conclusive evidence of the existence of the fourth has n found and its probable formula has been given.

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A THIRD METHYL ESTER OF PHTHALIC ACID.

BY C. G. ALLIN.

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hese experiments were undertaken under the direction of Professor an with the object of finding out whether it was possible to prepare ester of phthalic acid corresponding to the barium salt $H_4C_2O_4Ba)_4C_6H_4C_2O_3$. This barium salt was obtained by heating acid salt $(C_6H_4C_2O_4)_2H_2BaH_2O$ at 120–140° until constant weight was ained.

arium Salt and Ethyl Iodide.—(*a*) Five g. of the barium salt and 5 cc. yl iodide were shaken for several hours at room temperature.

b) Five g. of the barium salt and 5 cc. ethyl iodide with 3 cc. ethyl alco- were shaken for several hours at room temperature.

c) Five g. of the barium salt and 5 cc. ethyl iodide were heated at 100° two hours.

he contents of each of these tubes were then treated with water and ted for barium iodide with negative results in each case. This indi- ed that no ester had been formed.

arium Salt and Methyl Sulphate.—(*d*) 0.5 g. of the barium salt and c. methyl sulphate were shaken for four hours at room temperature. en the liquid was removed, the solid part was found to contain barium hate, which showed that a reaction had taken place.

e) Barium salt and methyl sulphate were heated in a sealed tube at ° for four hours and then filtered. Part of the filtrate was shaken h water to decompose the methyl sulphate but all the oil disappeared, ester being saponified by the sulphuric acid from the methyl sulphate. ther part of the filtrate, on standing, separated into two layers, one hich was found to contain much more sulphate than the other. The t containing least sulphate was washed with water, dried over sulphuric l and saponified with potassium hydroxide solution.

0.1500 gram of the oil required, 12.17 cc. potassium hydroxide sol.
Calculated for dimethyl phthalate, 16.13 cc.
Calculated for monomethyl phthalate, 18.59 cc.

s showed that this oil was, at any rate, not the pure ester correspond- to the barium salt, as the potassium hydroxide solution required to nify it would be intermediate between that required for the mono- hyl ester and that necessary for the dimethyl ester. Other experi- ts showed that when the neutral barium salt or the acid salt was heated with methyl sulphate the resulting liquid separated in each case into two layers.

(*f*) The barium salt and methyl sulphate were heated in a sealed tube for forty-five minutes. The liquid was filtered off hot and on cooling, a small quantity of white crystals separated out, which were washed free from methyl sulphate by benzene and recrystallized several times from ethyl acetate and finally gave a constant melting point of 187°. More of this product was obtained by washing the solid contents of the tube with ethyl acetate. That this substance is a compound of phthalic acid was shown by decomposing a small portion of it and obtaining the characteristic crystals of phthalic anhydride, but the melting point of monomethyl phthalate is 85° and dimethyl phthalate is a liquid.

Determination of the Methyl (Zeisel's Method).—0.2012 gram of the ester was heated with hydriodic acid in a current of carbon dioxide, the methyl iodide formed being passed into silver nitrate solution. Weight of silver nitrate formed = 0.4060 gram. Methyl found, 12.9 per cent. Calculated for $[C_6H_4(CO_2CH_3)_2]_4C_6H_4C_2O_3$, 13.0 per cent.

Determination of the Molecular Weight.—A molecular weight determination was made by finding the increase in the boiling point of acetone when the ester is dissolved in it.

Calculated for $[C_6H_4(CO_2CH_3)_2]_4C_6H_4C_2O_3$	924
Calculated for $[C_6H_4(CO_2CH_3)_2]_4C_6H_4C_2O_3/4$	231
Found	233

The substance was recovered from the acetone with unchanged melting point.

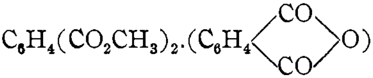
The most reasonable explanation of the molecular weight in acetone is that the ester is mostly dissociated into dimethyl phthalate and phthalic anhydride and recrystallizes from the acetone as the original ester. In that case, the easiest method of making the ester would be to dissolve these substances in acetone in the proper proportions and allow to crystallize.

0.21 g. of phthalic anhydride and 1.10 g. of dimethyl phthalate were dissolved in acetone and allowed to stand for half an hour. When the acetone was evaporated, the same weight of phthalic anhydride was found as was used and no crystals of the new ester. This shows conclusively that the ester is not dissociated into phthalic anhydride and dimethyl phthalate in acetone solution.

It is possible that the barium salt used might contain some of the salt $(C_6H_4C_2O_4)_5H_2Ba_4$ although there is no evidence that this is an intermediate stage in the preparation of the barium salt used in these experiments. If the ester were formed from this salt, it might be considered that the ester was a double compound of dimethyl phthalate and phthalic acid or of dimethyl phthalate and monomethyl phthalate, but attempts to obtain the ester by dissolving these substances in acetone and crystallizing gave the original materials only and none of the new ester. If the ester were derived as suggested, its formula would be

$$[C_6H_4(CO_2CH_3)_2]_4C_6H_4(CO_2H)_2 \div 4 = C_6H_4(CO_2CH_3)_2[C_6H_4(CO_2H_2)]_{\frac{1}{4}}$$

but with the data we have at present, the only formula which can be used is



$$C_6H_4(CO_2CH_3)_2.(C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O)_{\frac{1}{4}}.$$

It is hoped that measurement of the rate of saponification of dimethyl phthalate or of the rate of esterification of phthalic acid or of phthalic anhydride by methyl alcohol will show whether this new ester is an intermediate stage in one or more of these reactions.

Only about 0.6 g. of this ester has been prepared as the yield is very poor. This is probably due to the barium salt becoming protected by a layer of barium sulphate and it is hoped that some method of shaking the tube may increase the yield. Further investigation of this very interesting ester is in progress.

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NOTES ON CELLULOSE ESTERS.

BY R. G. WOODBRIDGE, JR.

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During the year 1907–8, the writer was engaged in the study of the chemistry of cellulose at the Massachusetts Institute of Technology, being the holder of a fellowship established for this purpose through the generosity of Mr. A. D. Little, of Boston. No limitations were placed upon the scope of the investigation except the wish of the donor that it should be of a scientific character rather than a search for results of immediate technical value. Attention was therefore mainly devoted to the study of reactions and derivatives of cellulose hitherto little known or inadequately described with the hope of throwing some light upon the chemical constitution of this important substance. As work progressed, several interesting questions presented themselves, some of which are now under investigation in the organic laboratory of the Institute. The present paper is devoted to the results of some work upon the propionates and formates of cellulose, which it is not expected to carry further at present.

Methods of Analysis.—In an investigation of this kind where it was constantly necessary to make analyses of esters prepared in various ways, the first essential was to possess a method for the determination of saponification values which should be rapid, reasonably accurate, and of such an experimental character that several determinations could be carried out at the same time.

It is well known that the method of saponification with boiling alcoholic