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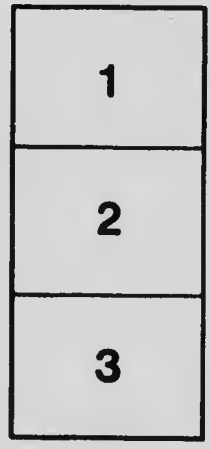

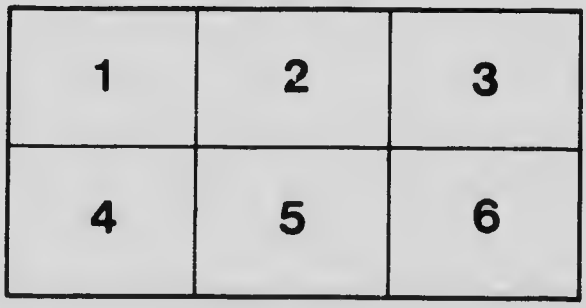

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PAPERS FROM THE CHEMICAL LABORATORIES

No. 88: A THIRD METHYL ESTER OF PHTHALIC ACID, BY C. G. ALLIN

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A Third Methyl Ester of Phthalic Acid.

By C. G. Allin.

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A THIRD METHYL ESTER OF PHTHALIC ACID.

By C. G. Allin.

Received July 12, 1909.

These experiments were undertaken under the direction of Professor Allan with the object of finding out whether it was possible to prepare an ester of phthalic acid corresponding to the barium salt $(C_8H_4C_2O_4Ba)_4C_8H_4C_2O_3$. This barinm salt was obtained by heating the acid salt $(C_8H_4C_2O_4)_2H_2BaH_2O$ at 120–140° until constant weight was obtained.

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

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

The contents of each of these tubes were then treated with water and tested for barium iodide with negative results in each case. This indicated that no ester had been formed.

Barium Salt and Methyl Sulphate.—(*d*) 0.5 g. of the barium salt and 5 cc. methyl sulphate were shaken for four hours at room temperature. When the liquid was removed, the solid part was found to contain barium sulphate, which showed that a reaction had taken place.

(*e*) Barium salt and methyl sulphate were heated in a sealed tube at 100° for four hours and then filtered. Part of the filtrate was shaken with water to decompose the methyl sulphate but all the oil disappeared, the ester being saponified by the sulphuric acid from the methyl sulphate. Another part of the filtrate, on standing, separated into two layers, one of which was found to contain much more sulphate than the other. The part containing least sulphate was washed with water, dried over sulphuric acid 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.

This showed that this oil was, at any rate, not the pure ester corresponding to the barium salt, as the potassium hydroxide solution required to saponify it would be intermediate between that required for the monomethyl ester and that necessary for the dimethyl ester. Other experiments 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, 1.9 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

$[C_6H_4(CO_2CH_3)_2]_4C_6H_4(CO_2H_2) + 4 = [C_6H_4(CO_2CH_3)_2]_2[C_6H_4(CO_2H_2)]_2$

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

$$C_6H_4(CO_2CH_3)_2.(C_6H_4\begin{matrix}CO\\ \diagup\diagdown\\ CO\end{matrix}O)_4.$$

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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