XCII.—*Aromatic Compounds obtained from the Hydroaromatic Series. Part II. The Action of Phosphorus Pentachloride on Trimethyldihydroresorcin.*

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IN 1901, Crossley (*Trans.*, **79**, 144) described a solid melting at $76\cdot5^{\circ}$, obtained by the action of phosphorus pentachloride on trimethyldihydroresorcin (I), and suggested that it was 3:5-dichloro-1:1:2-trimethyl- $\Delta^{2:4}$ -dihydrobenzene (II):

At a later period (*Trans.*, 1902, **81**, 826) it was shown that phosphorus pentachloride acts on dimethyldihydroresorcin (III) to give 3:5-dichloro-1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (IV), but that a

secondary reaction also takes place, consisting in the transformation of this hydroaromatic dichloride into 3:5-dichloro-*o*-xylene (V) (*Trans.*, 1902, **81**, 1543). It was therefore thought desirable to investigate further the action of phosphorus pentachloride on trimethyldihydroresorcin, and in 1903 (*Proc.*, **19**, 227) a short notice was published, in which it was indicated that, during the reaction, two substances are produced, a liquid, which is 3:5-dichloro-1:1:2-trimethyl- $\Delta^{2:4}$ -dihydrobenzene (VI), and the solid melting at $76\cdot5^{\circ}$, which belongs to the aromatic series and is 3:5-dichloro-1:2:6-trimethylbenzene (VII).

The former boils at $118\text{--}119^{\circ}$ (33 mm.), and its hydroaromatic nature is shown by the fact that it absorbs two atoms of bromine to form a very unstable dibromide, which readily loses two molecules of hydrogen bromide to form dichlorotrimethylbenzene (VII):

If, however, a large excess of bromine be used, then 3:5-dichloro-4-bromo-1:2:6-trimethylbenzene is formed,

This is an exactly similar behaviour to that of 3:5-dichloro-1:1-dimethyl- Δ -2:4-dihydrobenzene (VIII), which under the influence of bromine (Trans., 1904, 85, 264) is transformed into 3:5-dichloro-*o*-xylene (IX) or one of the two possible dichlorobromo-*o*-xylenes (X or XI) derivable from it :

A new point arises in discussing the constitution of dichlorotrimethyldihydrobenzene, for, unlike the corresponding dichloride obtained from dimethyldihydroresorcin, it is not a symmetrical molecule and may therefore be represented by one of the two following formulæ (XII or XIII) :

In order to obtain some evidence on this point, the substance was oxidised with potassium permanganate, when a mixture of dimethylmalonic and *as*-dimethylsuccinic acids was obtained. These acids could only be formed from a substance of formula XII, for from a

substance of formula XIII trimethylsuccinic acid should have resulted on oxidation, but no evidence of its formation could be obtained.

The solid melting at 76.5° , produced by the action of phosphorus pentachloride on trimethyldihydroresorcin would appear to be 3:5-dichloro-1:2:6-trimethylbenzene, for though there does not seem to be any ready method for directly orientating this substance, yet, arguing from analogy and taking into account its chemical behaviour, there can be little doubt that the above expression accurately describes its constitution.

In the first place, as pointed out on page 875, phosphorus pentachloride acts on dimethyldihydroresorcin to give 3:5-dichloro-1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (IV), which substance can be partially converted into 3:5-dichloro-*o*-xylene (V) by prolonged heating with phosphorus pentachloride. For this transformation to take place, a methyl group must wander into either an *ortho*- or a *para*-position:

but both in this case and in those of other derivatives of dimethyldihydroresorcin which have been examined (Trans., 1904, **85**, 264), no instance has been observed in which a methyl group has wandered into any but an *ortho*-position. It would seem therefore legitimate to conclude that in the case of 3:5-dichloro-1:1:2-trimethyl- $\Delta^{2:4}$ -dihydrobenzene (VI), where a methyl group might also wander into an *ortho*- or a *para*-position, the former would be selected and the resulting substance would be 3:5-dichloro-1:2:6-trimethylbenzene (VII).

One striking difference is observed in the behaviour of dimethyl- and of trimethyl-dihydroresorcin towards phosphorus pentachloride, and that is the comparative ease with which the corresponding hydroaromatic dichlorides are transformed into the aromatic derivatives. Thus, dimethyldihydroresorcin, when heated for two to three hours with phosphorus pentachloride, gives about 75 per cent. of the theoretical yield of the hydroaromatic and a comparatively small yield of the aromatic dichloride. The formation of the latter substance was indeed only observed after very careful fractionation of the accumulated high boiling residues from a large number of experiments.

Trimethyldihydroresorcin, on the other hand, under exactly the same conditions gives a product consisting of about one part of the liquid hydroaromatic and two parts (nearly 50 per cent. of the theoretical) of the solid aromatic dichloride.

The reaction was carried out under various conditions with the object of obtaining a better yield of the hydroaromatic dichloride, which was required for another research. The desired result was, however, not obtained, for if the amount of phosphorus pentachloride be decreased, or if the mixture be not heated for so long, the reaction does not complete itself, and the production of large quantities of dichlorotrimethyldihydrobenzene would appear to be impossible by this method, as the conditions necessary for its formation are also those under which it is transformed into dichlorotrimethylbenzene.

The last-mentioned substance is readily acted on by chlorine or bromine to give respectively trichloro- or dichloro-bromotrimethylbenzene; but it is extremely difficult to nitrate, probably owing to the fact that, no matter what conditions are adopted, the nitric acid acts principally as an oxidising agent.

3:5-Dichloro-4-nitro-1:2:6-trimethylbenzene,

can be obtained in small amount by pouring a solution of dichlorotrimethylbenzene in glacial acetic acid into fuming nitric acid. If, however, the conditions are slightly altered and fuming nitric acid is gradually added to an acetic acid solution of the aromatic derivative, a curious reaction takes place, resulting in the formation of a very small quantity of dichloronitrotrimethylbenzene and a much larger amount of trichlorotrimethylbenzene, $\text{CH}_3 \cdot \text{C} \begin{array}{c} \swarrow \text{C}(\text{CH}_3) \cdot \text{CCl} \\ \searrow \text{C}(\text{CH}_3) \cdot \text{CCl} \end{array} \cdot \text{CCl}$ (0.5 gram from 2 grams). The identity of this substance was established by analysis and by a mixed melting point with pure trichlorotrimethylbenzene, prepared by the direct chlorination of dichlorotrimethylbenzene. Presumably some of the dichlorotrimethylbenzene is first oxidised by the nitric acid, hydrochloric acid resulting, which in contact with nitric acid liberates chlorine, and this then causes substitution to take place.

When dichlorotrimethylbenzene is oxidised by nitric acid (sp. gr. 1.15) in sealed tubes, it is converted into a dichlorobenzenetricarboxylic acid, apparently 3:5-dichlorohemimellitic acid,

which resembles hemimellitic acid very closely in chemical properties (compare Graebe and Leonhardt, *Annalen*, 1896, 290, 217). Thus, on simply melting, it is transformed into its anhydride, which gives a particularly brilliant fluorescein reaction and yields an imide when ammonia is passed into it in the molten condition.

Experiments were carried out on the direct esterification of dichlorohemimellitic acid, as there seemed to be a possibility of thereby bring-

ing some direct evidence to bear on the constitution of the dichlorotrimethylbenzene from which it is derived. The latter substance might have one of the following formulæ :

according as to whether a methyl group had wandered into an *ortho*- or a *para*-position during its formation from dichlorotrimethyldihydrobenzene; hence the acid obtained from dichlorotrimethylbenzene on oxidation might be represented by :

But an acid of formula XIV should not be capable of direct esterification, for all the *ortho*-positions relative to the carboxyl group are occupied, whereas an acid of formula XV should give a mono-ester on direct esterification.

When the above acid was dissolved in methyl alcohol, the solution saturated with hydrogen chloride and allowed to stand for twelve hours, nothing but unchanged material was recovered; but on repeating the experiment and allowing to stand 120 hours, a few crystals (0.05 gram from 1 gram of acid) of a monomethyl ester were obtained. This ester was also produced in about the same amount by heating the acid for six hours with a four per cent. solution of sulphuric acid in methyl alcohol. It cannot therefore be said that dichlorohemimellitic acid is capable of direct esterification at all readily, and it would appear most probable that the formation of this small amount of ester is really due to the fact that the anhydride of the acid is first formed, and this is then converted into the ester by the boiling methyl alcohol. Graebe and Leonhardt (*ibid.*, p. 226) have shown that the best method for preparing the monomethyl ester of hemimellitic acid is by boiling the corresponding anhydride with methyl alcohol, and this also applies to the acid at present under consideration. When its anhydride is boiled with methyl alcohol, it is slowly converted into the monomethyl ester, one gram of anhydride giving 0.2 gram of the ester after boiling for thirty-two hours. All available evidence is therefore in favour of the substance being a dichlorohemimellitic acid having the constitution represented by formula XIV.

EXPERIMENTAL.

The action of phosphorus pentachloride on trimethyldihydroresorcin, as mentioned in the introduction, has been tried under very varied conditions, but it does not seem necessary to quote the details of more than one experiment.

Thirty grams (1 molecule) of trimethyldihydroresorcin and 80 grams of dry chloroform were placed in a flask attached to a reflux condenser, and 84 grams (2 molecules) of phosphorus pentachloride added, at first in small quantities, as a somewhat vigorous reaction sets in, and afterwards much more freely. The mixture was then heated on the water-bath for five hours, during which time a remarkable series of colour changes took place: the solution, at first yellowish-brown, became deep green, deep indigo-blue, bluish-black, and finally greenish-black. The reaction mixture was then slowly poured into 500 c.c. of water, being well shaken and cooled throughout, and the whole extracted three times with ether, the ethereal solution washed with dilute sodium hydroxide solution until no longer acid, then with water, dried over calcium chloride, and the ether evaporated.

The residue set to a mass of crystals (A=8 grams), which were collected at the pump and the yellow oily filtrate distilled, when at 36 mm., 10·4 grams passed over between 126° and 131°. The higher boiling fractions solidified almost completely on standing and yielded 8 grams of solid (B). The fraction 126—131° was then twice distilled, when a further quantity of solid (C) was obtained from the higher fractions, and 6·5 grams of a liquid boiling constantly at 118—119° (33 mm.), which on analysis gave the following numbers:

0·1255 gave 0·2611 CO₂ and 0·0716 H₂O. C=56·74; H=6·34.

0·1284 „ 0·1948 AgCl. Cl=37·53

C₉H₁₂Cl₂ requires C=56·54; H=6·28; Cl=37·17 per cent.

3:5-Dichloro-1:1:2-trimethyl-Δ^{2:4}-dihydrobenzene,

is an oily liquid boiling at 118—119° (33 mm). and possessing a camphoraceous odour. It is colourless when freshly distilled, but quickly becomes yellow; the colour deepens on standing and the whole slowly resinifies. On adding bromine to a solution of the substance in an equal volume of dry chloroform, the colour of the former is rapidly discharged and quantities of hydrogen bromide are evolved. If the addition of bromine be stopped as soon as the first signs of excess appear and the chloroform be evaporated, the residue partially solidifies. After spreading on a porous plate, the solid crystallised from methyl

alcohol in long, glistening needles, which melted at 76.5° and proved to be identical with the dichlorotrimethylbenzene described below. If, however, a large excess of bromine be added to the chloroform solution, or if bromine be added directly to dichlorotrimethyldihydrobenzene, it is slowly absorbed and hydrogen bromide evolved. The solid residue separated from absolute ethyl alcohol in silky needles melting at $222-223^{\circ}$, identical in every respect with the dichlorobromotrimethylbenzene described on page 882.

Oxidation of Dichlorotrimethyldihydrobenzene.—Nine grams of the dichloride were suspended in 150 c.c. of water, the whole heated on a water-bath in a flask attached to a reflux condenser, and a cold saturated solution of potassium permanganate gradually added. Oxidation took place very slowly and required about sixty hours for completion. The product was separated from manganese dioxide, evaporated to a small bulk, acidified with dilute sulphuric acid, and extracted six times with ether, when, after evaporation of the ether, a syrupy residue smelling strongly of acetic acid was obtained. After standing some time in a vacuum desiccator over sulphuric acid, it partially solidified and was spread on a porous plate. The white solid obtained in this way softened at 105° , melted at $115-120^{\circ}$, and evolved gas at $160-165^{\circ}$. This is the behaviour of a mixture of dimethylmalonic and *as*-dimethylsuccinic acids (compare Trans., 1905, 87, 1499), of which the substance was proved to consist in the following manner. It was heated until no more carbon dioxide was evolved, during which time a liquid with the unmistakable odour of isobutyric acid was evolved; the residue was dissolved in boiling water and the solution saturated with hydrogen chloride, when needle-shaped crystals separated, which melted at 140° , nor was this melting point altered on mixing with pure *as*-dimethylsuccinic acid.

A portion of the acid was then boiled with acetyl chloride, and the anhydride so obtained converted into the anilic acid in the usual manner; this was found to crystallise from methyl alcohol in nacreous, scaly needles melting at $186-187^{\circ}$ with evolution of gas, and after mixing the substance with pure dimethylsuccinanilic acid no change in the melting point was observed.

The crystalline residues A, B, and C (see page 880) were purified by crystallisation from absolute methyl alcohol and analysed:

0.1048 gave 0.2188 CO_2 and 0.0506 H_2O . C = 56.94; H = 5.36.

0.1376 „ 0.2872 CO_2 „ 0.0680 H_2O . C = 56.92; H = 5.49.

0.1410 „ 0.2147 AgCl . Cl = 37.66.

0.1610 „ 0.2439 AgCl . Cl = 37.48.

$\text{C}_9\text{H}_{10}\text{Cl}_2$ requires C = 57.14; H = 5.30; Cl = 37.56 per cent.

3 : 5-Dichloro-1 : 2 : 6-trimethylbenzene, $\text{CH}_3 \cdot \text{C} \begin{smallmatrix} \text{C}(\text{CH}_3) \cdot \text{CCl} \\ \text{C}(\text{CH}_3) \cdot \text{CCl} \end{smallmatrix} \text{CH}$, is

readily soluble in the cold in chloroform, benzene, acetone, ethyl acetate, or light petroleum (b. p. 80—100°) and crystallises from ethyl or, better, methyl alcohol in glistening needles, frequently, when using the latter solvent, 3 to 4 inches in length, and melting at 76·5°. A chloroform solution of bromine was not decolorised by the addition of dichlorotrimethylbenzene, but on dissolving the latter substance in the smallest possible quantity of chloroform, adding a trace of iron filings and then bromine, substitution took place readily after slight warming, and the whole set to a solid mass, which was purified by crystallisation from ethyl alcohol and analysed :

0·1044 gave 0·1860 Ag haloids and 0·1266 Ag. Cl=26·25 ; Br=30·60.

$C_9H_9Cl_2Br$ requires Cl=26·49 ; Br=29·84 per cent.

3 : 5-Dichloro-4-bromo-1 : 2 : 6-trimethylbenzene,

is readily soluble in the cold in chloroform, somewhat less so in acetone, benzene, or ethyl acetate, and crystallises from absolute ethyl alcohol in long, silky needles melting at 222—223°. When acted on with fuming nitric acid, it yields a small amount of a nitrogenous body, crystallising from alcohol in yellow, flattened needles melting at 170—171°, which was thought to be 3 : 5-dichloro-4-nitro-1 : 2 : 6-trimethylbenzene (see page 883), but a mixture of these two substances melted at 140°, and as the body melting at 171° was produced in such small amount, it was impossible to investigate its nature further.

3 : 4 : 5-Trichloro-1 : 2 : 6-trimethylbenzene was obtained by dissolving dichlorotrimethylbenzene in the smallest possible quantity of chloroform, adding a trace of iron filings, and then passing dry chlorine into the solution. It is readily soluble in the cold in benzene or chloroform, crystallises from alcohol, acetone, or ethyl acetate in silky needles melting at 217—218°, and sublimes in long, glistening needles.

0·1004 gave 0·1931 AgCl. Cl=47·58.

$C_9H_9Cl_3$ requires Cl=47·65 per cent.

Action of Nitric Acid on Dichlorotrimethylbenzene.—Two grams of dichlorotrimethylbenzene were powdered and added to 15 c.c. of glacial acetic acid, an insufficient amount for complete solution in the cold, and 16 c.c. of fuming nitric acid gradually dropped into the solution, when a slight amount of heat was evolved, and nearly the whole of the solid dissolved. When all the nitric acid had been added, there was a sudden separation of solid matter (0·5 gram), which was filtered (filtrate=A) after allowing the whole to stand for

several hours. This solid crystallised from ethyl acetate in silky needles melting at 217—218°, nor was this melting point altered on mixing with pure 3:4:5-trichloro-1:2:6-trimethylbenzene (see page 882). The identity of the two substances was further proved by a chlorine determination.

0.1016 gave 0.1952 AgCl. Cl = 47.52.

$C_9H_5Cl_3$ requires Cl = 47.65 per cent.

The filtrate A (see p. 882) was poured into water, when a very viscid semi-solid separated. This, together with material obtained in similar experiments, representing in all 8 grams of dichlorotrimethylbenzene, was dissolved in absolute alcohol, when, on cooling, 0.3 gram of silky needles separated, melting at 175—176°, and a mixed melting point proved that they were identical with 3:5-dichloro-4-nitro-1:2:6-trimethylbenzene described below.

In another experiment, 1 gram of dichlorotrimethylbenzene was dissolved in glacial acetic acid by slightly heating and the solution slowly poured into 10 c.c. of fuming nitric acid. After the addition, the whole was gently warmed on the water-bath until all the solid had gone into solution and then allowed to stand for twelve hours, when long, needle-shaped crystals separated (0.2 gram), which were filtered (filtrate = A), and after purification the nitrogen was determined:

0.2105 gave 10 c.c. moist nitrogen at 11° and 760 mm. N = 5.66.

$C_9H_5O_2NCl_2$ requires N = 5.98 per cent.

3:5-Dichloro-4-nitro-1:2:6-trimethylbenzene,

is readily soluble in the cold in acetone, benzene, or chloroform and crystallises from ethyl acetate or alcohol in long, faintly yellow, silky needles melting at 175—176°.

On pouring the above-mentioned filtrate A into water, a very viscous solid (0.2 gram) separated, from which, on treatment with alcohol, a further small quantity of the nitro-product was obtained. This derivative is also produced in minute amounts by the action of a nitrating mixture on dichlorotrimethylbenzene.

Oxidation of Dichlorotrimethylbenzene.

Dichlorotrimethylbenzene, in quantities of 2 grams at a time, was heated with 16 c.c. of nitric acid (sp. gr. 1.15) in a sealed tube for five to six hours at 170—180°. The liquid contents of the tube were then evaporated to dryness on the water-bath, purified by crystallisation

from water saturated with hydrogen chloride, and analysed after drying in a vacuum over potassium hydroxide :

0.1548 gave 0.2189 CO_2 and 0.0244 H_2O . $\text{C} = 38.56$; $\text{H} = 1.75$.

0.1332 „ 0.1356 AgCl . $\text{Cl} = 25.18$.

$\text{C}_9\text{H}_4\text{O}_6\text{Cl}_2$ requires $\text{C} = 38.71$; $\text{H} = 1.43$; $\text{Cl} = 25.43$ per cent.

Dichlorohemimellitic acid (3:5-dichlorobenzene-1:2:6-tricarboxylic acid), $\text{CO}_2\text{H} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{CO}_2\text{H}) \cdot \text{CCl} \\ \text{C}(\text{CO}_2\text{H}) \cdot \text{CCl} \end{smallmatrix} \text{CH}$, of which the yield is practically theoretical, is insoluble in benzene or chloroform, readily soluble in the cold in water, ethyl alcohol, acetone, ether, or ethyl acetate, and crystallises from water saturated with hydrogen chloride in clusters of short, colourless needles, melting at $226-227^\circ$, with previous softening and contraction in bulk. It can also be crystallised by the slow evaporation of its aqueous solution, when it separates in transparent, glistening, hexagonal plates, which finally melt at $226-227^\circ$, but with more softening and contraction in bulk than when the acid is crystallised from hydrochloric acid. These crystals contain two molecules of water, which they readily lose on heating to 100° .

0.5792 lost 0.0660. $\text{H}_2\text{O} = 11.39$.

$\text{C}_9\text{H}_4\text{O}_6\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.42$ per cent.

The molecular weight of the acid was determined by titration with potassium hydroxide, using phenolphthalein as indicator, and also by analysis of its silver salt (see page 885) :

0.2817 required 30.6 c.c. $N/10$ $\text{KOH} = 0.1713$ KOH .

Molecular weight, found 276.2 ; calculated 279.

When the acid is heated with resorcinol and a drop of sulphuric acid, the mixture dissolved in sodium hydroxide and poured into water, a red solution with a particularly brilliant green fluorescence is obtained. If a solution of potassium chloride be added to a concentrated aqueous solution of the acid and the whole allowed to stand, well-formed, transparent, flattened needles separate, and it was thought that this would be the acid potassium salt, and that dichlorohemimellitic acid behaved like hemimellitic acid (compare Graebe and Leonhardt, *Annalen*, 1896, 290, 217) itself in this respect. But although the crystals contained potassium, the amount was insufficient for even a monopotassium acid salt, and apparently a solution sufficiently concentrated for this salt to separate is also concentrated enough for the acid to crystallise out to some extent.

The silver salt, prepared in the usual manner, is a white, caseous precipitate.

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0.1446 gave 0.0781 Ag. Ag = 54.01.

 $C_9HO_6Cl_2Ag_3$ requires Ag = 54.0 per cent.

Molecular weight of acid, found 278.9; calculated 279.

The *anhydride* is most easily obtained by heating the acid to 235—240° for a few minutes, and a specimen produced in this way was analysed without any further purification:

0.1154 gave 0.1740 CO_2 and 0.0124 H_2O . C = 41.12; H = 1.19. $C_9H_2O_5Cl_2$ requires C = 41.37; H = 0.76 per cent.

This substance can also be prepared by dissolving the acid in acetic anhydride, from which it crystallises on standing. The anhydride, which sublimes in fern-like aggregates of flattened needles, is readily soluble in the cold in water to give an acid solution, it is also soluble in ethyl alcohol, acetone, or ethyl acetate, and is insoluble in benzene, chloroform, or light petroleum. It crystallises from acetic anhydride in nodules consisting of stellar aggregates of very fine needles, which melt sharply at 227—228°. Evidently the final melting point of dichlorohemimellitic acid is really the melting point of its anhydride, the previous softening and contraction in bulk being due to anhydride formation.

The *imide* prepared by passing ammonia into the molten anhydride crystallised from water in nodules of microscopic crystals, which melted at 253—254°.

0.2407 gave 11.4 c.c. moist nitrogen at 12° and 770 mm. N = 5.69.

 $C_9H_3O_4NCl_2$ requires N = 5.39 per cent.

Esterification of Dichlorohemimellitic Acid.

The *trimethyl* ester may be prepared in quantitative amount by heating the silver salt in benzene suspension with the calculated amount of methyl iodide. It is insoluble in cold water or potassium hydroxide solution, readily soluble in the cold in chloroform, ethyl acetate or acetone, and crystallises from methyl alcohol or, better, from light petroleum (b. p. 40—60°) in glistening, transparent rhombohedra melting at 62—63°.

0.1154 gave 0.1902 CO_2 and 0.0371 H_2O . C = 44.94; H = 3.57. $C_{12}H_{10}O_6Cl_2$ requires C = 44.86; H = 3.11 per cent.

Action of Methyl Alcohol on the Anhydride.—A solution of 1 gram of the anhydride in methyl alcohol was heated to the boiling point for thirty-two hours, when the residue obtained on evaporation slowly solidified. It dissolved for the most part readily in water and probably consisted largely of unchanged anhydride, but a small portion would not dissolve without boiling the solution, which, when allowed to evapo-

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rate slowly in a vacuum, deposited radiating clusters of needles, readily soluble in cold potassium hydroxide solution. These were purified by crystallisation from water, when nacreous, scaly needles separated, melting at 141—142°, with a previous distinct contraction in bulk at 88—90°. On analysis, the following figures were obtained :

0·1008 gave 0·1500 CO₂ and 0·0262 H₂O. C = 40·58 ; H = 2·88.

C₁₀H₆O₆Cl₂ requires C = 40·95 ; H = 2·05 per cent.

Although these numbers do not agree so closely as could be desired, they show conclusively that the substance is the monomethyl ester of dichlorohemimellitic acid ; but the amount obtained was so small as not to permit a further purification.

The mother liquors from the analysed material deposited a few small transparent cubes, which melted sharply at 141—142° without any previous contraction, and were probably the pure monomethyl ester.

This same ester was formed by submitting dichlorohemimellitic acid to Fischer and Speyer's esterification method, and also by saturating a methyl-alcoholic solution of the acid with hydrogen chloride and allowing it to stand for 120 hours. The former method gave rather more of the ester than the latter, but in both cases the amount was very small and much less than is produced by boiling the anhydride with methyl alcohol.

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