CLV.—*Researches on Anthraquinones and Phthaleins.*

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OF the fourteen possible hydroxymethylantraquinones, only three are known with any degree of certainty, namely, the 4 : 1-, 3 : 2-, and 3 : 1-derivatives, which have been prepared from *p*-, *o*-, and *m*-cresol respectively :

In addition, another has been described by Römer and Link (*Ber.*, 1883, **16**, 700), who obtained it from amino-2-methylantraquinone, but were unable to determine its constitution. As the subject possessed considerable interest for us, we determined to prepare derivatives of this series by the action of aluminium chloride on a mixture of phthalic anhydride and the cresol methyl ethers, a reaction resulting in the formation of derivatives of benzoylbenzoic acid, which when heated with concentrated sulphuric acid condense to derivatives of anthraquinone :

This reaction was employed by Nourrisson (*Ber.*, 1886, **19**, 2103) for the preparation of *p*-methoxybenzoylbenzoic acid and of 2-methoxy-anthraquinone from phthalic anhydride and anisole.

In the condensation with sulphuric acid to the quinone, it was usually found that a certain amount of the methoxy-compound had suffered hydrolysis, so that hydroxymethylantraquinone was also obtained. At the same time, we discovered that phthalic acid could be directly condensed with the cresols by means of boric acid, and in this way hydroxymethylbenzoylbenzoic acids were prepared, which on further treatment with sulphuric acid yielded hydroxymethylantraquinone :

It is quite apparent that from *p*-cresol, only one hydroxymethyl-anthraquinone could result from either method of condensation, and such proved to be the case, but the products from *o*- and *m*-cresol were much more interesting, inasmuch as they differed according to the method of preparation. Thus, when *o*-cresol is condensed with boric acid, the hydroxymethylanthraquinone finally obtained melted at 185—186°, whereas the product furnished by the aluminium chloride method melted above 300°, neither of them being identical with that prepared by Fraude (*Annalen*, 1880, 202, 165) from *o*-cresol, namely,

which melts at 260—262°. The possible formulæ for our two new hydroxymethylanthraquinones are therefore:

and we venture to assign the first formula to the product obtained from the boric acid condensation and the second to that from the aluminium chloride condensation on the following grounds. When phthalic anhydride and anisole are condensed by means of aluminium chloride, the anisole is substituted in the para-position with regard to the methoxyl group, and as it can be fairly safely assumed that *o*-cresol methyl ether would act similarly to anisole the formula of the intermediate acid is

This acid, on further condensation and hydrolysis, can give rise to two different quinones, namely,

The second is already known (Fraude, *loc. cit.*), so that the first is the

formula of the hydroxymethylantraquinone (m. p. above 300°) prepared by the aluminium chloride method. The remaining formula,

must therefore represent the hydroxymethylantraquinone (m. p. $185-186^{\circ}$) from the boric acid condensation product. This would indicate that boric acid promotes condensation in the ortho-position with respect to the hydroxyl group, and this is well exemplified in the condensation of phthalic anhydride with α -naphthol in presence of boric acid, when substitution in the naphthol nucleus takes place almost exclusively in the ortho-position with respect to the hydroxyl group. Nevertheless, in the case of *o*-cresol, the production of some *o*-cresolphthalein shows that the para-position is also attacked.

As *m*-cresol can only give rise to two hydroxymethylantraquinones,

the second of which is known and melts at $299-300^{\circ}$ (Bistrzycki and Yssel de Schepper, *Ber.*, 1898, **31**, 2790), the products of our reaction should have been easily identified. This was so in the case of the boric acid condensation product, which behaved quite normally, yielding a hydroxymethylantraquinone (m. p. 178°) which in all probability is identical with that prepared by Römer and Link (*Ber.*, 1883, **16**, 700) from amino-2-methylantraquinone, who found practically the same melting point, namely, $177-178^{\circ}$. The reaction, in conformity with our rule that boric acid promotes the ortho-substitution, can be expressed thus:

The condensation with aluminium chloride, however, gave very confusing results. The intermediate acid melted at a very low temperature (61°), and when treated with concentrated sulphuric acid gave an exceedingly poor yield of methoxy- and hydroxy-methylantraquinone, the latter having rather a low melting point (150°). In view

of these facts, we are of the opinion that the intermediate acid consists mainly of 2'-methoxy-6'-methylbenzoylbenzoic acid,

mixed with one or both of the other possible isomerides,

and that the hydroxymethylanthraquinone melting at 150° is a mixture.

In addition to the cresols, *m*-4-xyleneol and its methyl ether have been condensed with phthalic acid by the two methods at our disposal: hydroxydimethylanthraquinone being obtained in one case and methoxydimethylanthraquinone in the other. From a consideration of the formula of *m*-4-xyleneol,

it is evident that the constitutions of these two quinones are

but we have not been able to prove that one is the methyl ether of the other, as we found it impossible to methylate the hydroxy-compound, and the methoxy-derivative is only hydrolysed by sulphuric acid with difficulty, this process also being attended with considerable decomposition.

In addition to the derivatives of benzoylbenzoic acid, there were usually obtained by the boric acid condensations the corresponding fluorans, which are characterised by their fluorescence in concentrated sulphuric acid solution.

By means of boric acid, 4-hydroxyphthalic acid was also condensed with the cresols and *m*-4-xyleneol. In the case of *o*-cresol, it was only possible to isolate the hydroxycresolphthalein, but from *m*- and *p*-cresols the corresponding benzoylbenzoic acids, the fluorans, and the anthraquinones were all prepared. Indeed, in the case of *m*-cresol, there was evidence that two series of these substances were to be obtained, although we were only successful in isolating one series in the pure state. The experiment with *m*-4-xyleneol was interesting

from the fact that the anthraquinone was obtained directly from the boric acid fusion and that no fluoran was found.

Several experiments were also conducted on the boric acid condensation of phthalic acid with other para-substituted phenols. Quinol and toluquinol did not yield the intermediate acids, but formed directly the corresponding quinizarin and methylquinizarin respectively.

Experiments with bromo-*o*-cresol and bromo-*p*-cresol resulted in the elimination of hydrogen bromide and the formation of dihydroxy-methylantraquinones, which, however, were not obtained sufficiently pure for analysis.

Diphenol and dinaphthol were also found to give condensation products, a description of which will be reserved for a future communication.

At the end of this paper, an account is given of some experiments on the condensation of succinic and maleic anhydrides on cresol methyl ether in presence of aluminium chloride. The acids prepared have probably the following constitutions :

but no success has yet attended our efforts to effect further condensation without decomposition.

EXPERIMENTAL.

Condensations with Aluminium Chloride.

*4'-Methoxy-5'-methyl-2-benzoylbenzoic acid,**

—Aluminium chloride (240 grams) is added in three portions to a mixture of *o*-cresol methyl ether (200 grams) and phthalic anhydride (240 grams) in carbon disulphide, and the whole heated on the water-bath for ten to fifteen hours. After decanting the carbon disulphide, the hard product is treated with a large quantity of ice and hydrochloric acid, whereby the acid is obtained as an oily mass. Volatile impurities are removed by steam, and the residue is dissolved in sodium carbonate and reprecipitated with hydrochloric acid, being finally crystallised from methyl alcohol, from which it separates as a white powder melting at 176°:

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0.1418 gave 0.3680 CO₂ and 0.0653 H₂O. C=70.77; H=5.11.

C₁₆H₁₄O₄ requires C=71.11; H=5.18 per cent.

4'-Methoxy-5'-methyl-2-benzoylbenzoic acid is soluble in alcohol, acetic acid, ether, or benzene, but very sparingly so in hot water. When heated in glacial acetic acid with one molecular equivalent of bromine, it yields the monobromo-derivative, which is obtained as an oil on pouring the product in water; it is dissolved in sodium carbonate, reprecipitated with acid, and crystallised from glacial acetic acid, from which it separates in yellow needles melting at 219–220°:

0.1230 gave 0.2666 CO₂ and 0.0450 H₂O. C=55.08; H=3.78.

0.1240 „ 0.3797 AgBr. Br=22.8.

C₁₆H₁₃O₄Br requires C=55.01; H=3.44; Br=22.9 per cent.

Bromo-4-methoxy-5'-methyl-2-benzoylbenzoic acid is soluble in alcohol or acetic acid; it dissolves in concentrated sulphuric acid forming a red solution, which becomes darker on heating, and a compound is produced which is probably bromomethoxymethylanthraquinone,

This crystallises from alcohol in greenish-yellow needles melting at 179–180°.

2-Methoxy-1-methylanthraquinone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_2\text{Me}\cdot\text{OMe}$, is produced when 4'-methoxy-5'-methyl-2-benzoylbenzoic acid is heated to 155° in concentrated sulphuric acid. The formation of the quinone is indicated by the solution becoming intensely red, and on pouring the product into cold water a yellow precipitate is obtained. This is collected, well washed with hot dilute potassium hydroxide to remove the hydrolysed quinone, and crystallised from methyl alcohol, from which it separates in canary-yellow needles melting at 184° and subliming somewhat readily:

0.1187 gave 0.3305 CO₂ and 0.0507 H₂O. C=75.93; H=4.74.

C₁₆H₁₂O₃ requires C=76.19; H=4.76 per cent.

2-Methoxy-1-methylanthraquinone is soluble in acetic acid or alcohol; its solution in concentrated sulphuric acid is scarlet.

2-Hydroxy-1-methylanthraquinone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_2\text{Me}\cdot\text{OH}$, is precipitated when the alkaline liquors from the foregoing quinone are acidified. It crystallises from glacial acetic acid in yellow needles melting above 300°:

0.1293 gave 0.3565 CO₂ and 0.0493 H₂O. C=75.19; H=4.24.

C₁₅H₁₀O₃ requires C=75.63; H=4.20 per cent.

2-Hydroxy-1-methylanthraquinone dissolves in alcohol or benzene;

its *potassium* salt is sparingly soluble in cold water with a reddish-violet colour.

Monobromo-2-methoxy-1-methylantraquinone is prepared by heating a solution of 2-methoxy-1-methylantraquinone in glacial acetic acid with one molecular proportion of bromine on the water-bath until the bromine has disappeared. The bromo-compound which separates out on cooling, crystallises from glacial acetic acid in yellow needles melting at 228°:

0.1027 gave 0.2178 CO₂ and 0.0303 H₂O. C = 57.83; H = 3.27.

0.1130 „ 0.0643 AgBr. Br = 24.3.

C₁₆H₁₁O₃Br requires C = 58.00; H = 3.32; Br = 24.1 per cent.

Bromo-2-methoxy-1-methylantraquinone is sparingly soluble in alcohol, and dissolves in sulphuric acid with a red colour which on heating changes to brown.

Mononitro-2-methoxy-1-methylantraquinone is formed when 2-methoxy-1-methylantraquinone is dissolved in cold fuming nitric acid. The product is poured into water, the precipitate washed with water and afterwards with dilute potassium hydroxide, and crystallised with acetic acid, from which it separates in canary-yellow needles which melt at 179°:

0.1537 gave 6.2 c.c. nitrogen at 17° and 762 mm. N = 4.7.

C₁₆H₁₁O₅N requires N = 4.7 per cent.

Mononitro-2-methoxy-1-methylantraquinone dissolves in cold concentrated sulphuric acid forming an orange-red solution which becomes blood-red on heating. When treated with stannous chloride and potassium hydroxide, it is reduced to *amino-2-methoxy-1-methylantraquinone*, which crystallises from methyl alcohol in bright red needles melting at 181°, and forms a *hydrochloride* which decomposes in water. On boiling with acetic anhydride, the amino-compound yields *acetyl-amino-2-methoxy-1-methylantraquinone*, which crystallises from glacial acetic acid in brown needles melting at 204°:

0.1423 gave 0.3649 CO₂ and 0.0616 H₂O. C = 69.93; H = 4.79.

0.1870 gave 7.2 c.c. nitrogen at 16° and 767 mm. N = 4.53.

C₁₈H₁₅O₄N requires C = 69.92; H = 4.85; N = 4.53 per cent.

It forms a pale red solution with sulphuric acid.

Mononitro-2-hydroxy-1-methylantraquinone.—This substance is also produced in the nitration of methoxymethylantraquinone owing to hydrolysis of the methoxyl group, and is obtained from the alkaline wash water by precipitation with hydrochloric acid. It crystallises from acetic acid in pale yellow, feathery needles melting at 167—168°:

0.1358 gave 5.7 c.c. nitrogen at 18° and 764 mm. N = 4.85.

C₁₅H₉O₅N requires N = 4.9 per cent.

Mononitro-2-hydroxy-1-methylanthraquinone dissolves in sulphuric acid with a carmine, and in alkalis with a brown, colour.

Trinitro-2-methoxy-1-methylanthraquinone is formed when an excess of fuming nitric acid is added to a solution of 2-methoxy-1-methylanthraquinone in sulphuric acid and the mixture allowed to stand for several hours. The product is isolated in the same manner as the mononitro-derivative. It separates from glacial acetic acid as a buff-coloured powder melting at 212° with decomposition :

0.2095 gave 19.2 c.c. nitrogen at 17° and 771 mm. $N = 10.8$.

$C_{16}H_9O_9N_3$ requires $N = 10.8$ per cent.

Trinitro-2-methoxy-1-methylanthraquinone is sparingly soluble in alcohol or cold sulphuric acid. In warm sulphuric acid it dissolves with a brown colour.

[With JOHN HAROLD ANDREW.]

2'-Methoxy-5'-methyl-2-benzoylbenzoic acid,

is prepared from *p*-cresol methyl ether in the same manner as 4'-methoxy-5'-methyl-2-benzoylbenzoic acid from *o*-cresol methyl ether. It is soluble in alcohol, ether, or acetic acid, and sparingly so in water ; it melts at 122° :

Found, $C = 71.05$; $H = 5.11$.

$C_{16}H_{14}O_4$ requires $C = 71.11$; $H = 5.18$ per cent.

When heated to 150° with concentrated sulphuric acid, this acid condenses to

4-Methoxy-1-methylanthraquinone, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_2Me \cdot OMe$, which is isolated and purified exactly like 2-methoxy-1-methylanthraquinone. It crystallises from methyl alcohol in orange-yellow needles which melt at 170 — 171° :

$C = 75.95$; $H = 4.91$.

$C_{16}H_{12}O_3$ requires $C = 76.19$; $H = 4.76$ per cent.

When strongly heated with concentrated sulphuric acid, hydrolysis occurs with the formation of 4-hydroxy-1-methylanthraquinone, which crystallises in yellow needles melting at 175° (Birukoff, *Ber.*, 1887, 20, 2069, gives 179 — 170°) :

0.1492 gave 0.4134 CO_2 and 0.0583 H_2O . $C = 75.57$; $H = 4.33$.

$C_{15}H_{10}O_3$ requires $C = 75.63$; $H = 4.20$ per cent.

[With CLAUDE VAZEILLE TEMPERLEY.]

4(5): 2'-Dimethoxy-5'-methyl-2-benzoylbenzoic acid,
 $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OMe}.$

—The acid is prepared from 4-methoxyphthalic anhydride and *p*-cresol methyl ether by the same process as used for 4'-methoxy-5'-methyl-2-benzoylbenzoic acid; it is best purified by repeated crystallisation from water, in which it is very sparingly soluble. It dissolves in alcohol, chloroform, or acetic acid, and melts at 157.5° :

0.1927 gave 0.4802 CO_2 and 0.0933 H_2O . $\text{C} = 67.96$; $\text{H} = 5.38$.

$\text{C}_{17}\text{H}_{16}\text{O}_5$ requires $\text{C} = 68.00$; $\text{H} = 5.33$ per cent.

When heated to 110° with concentrated sulphuric acid, it undergoes condensation and partial hydrolysis, yielding probably 6(7)-hydroxy-4-methoxy-1-methylanthraquinone, $\text{HO} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2\text{Me} \cdot \text{OMe}$, which crystallises in yellow needles melting at 158° :

0.1176 gave 0.3070 CO_2 and 0.0490 H_2O . $\text{C} = 71.19$; $\text{H} = 4.63$.

$\text{C}_{16}\text{H}_{12}\text{O}_4$ requires $\text{C} = 71.64$; $\text{H} = 4.48$ per cent.

The presence of one methoxyl group was also confirmed by an estimation by Zeisel's method:

Found, $\text{OMe} = 11.40$.

$\text{C}_{15}\text{H}_9\text{O}_3 \cdot \text{OMe}$ requires $\text{OMe} = 11.55$ per cent.

This quinone is readily soluble in alcohol, but only sparingly so in light petroleum or carbon disulphide. With potassium hydroxide it yields a deep red-coloured potassium salt.

4:6(7)-Dimethoxy-1-methylanthraquinone,

is obtained by dissolving 4(5): 2'-dimethoxy-5'-methyl-2-benzoylbenzoic acid together with a little boric acid in cold concentrated sulphuric acid and carefully adding fuming sulphuric acid (containing 60 per cent. of sulphur trioxide) so that the temperature does not rise above 40° . The product is poured into ice-water, the precipitate collected, washed, and crystallised from acetic acid. It melts at 141° , does not dissolve in dilute aqueous potassium hydroxide, and is distinguished from the foregoing quinone by its ready solubility in carbon disulphide.

2'-Methoxy-3':5'-dimethyl-2-benzoylbenzoic acid,

is prepared from *m*-4-xyleneol methyl ether in the same way as 4'-methoxy-5'-methyl-2-benzoylbenzoic acid is prepared from *o*-cresol methyl ether. It melts at $188-189^\circ$:

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0.1815 gave 0.4758 CO₂ and 0.0914 H₂O. C=71.49; H=5.58.

C₁₇H₁₆O₄ requires C=71.83; H=5.63 per cent.

2'-Methoxy-3':5'-dimethyl-2-benzoylbenzoic acid is very soluble in alcohol or acetic acid, but only moderately so in benzene. It dissolves in cold sulphuric acid giving a dirty green solution, which on heating turns red owing to the formation of:

4-Methoxy-1:3-dimethylantraquinone, C₆H₄ $\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}$ C₆HMe₂·OMe.—

This quinone is isolated in the usual manner and, after crystallisation from acetic acid, melts at 176—177°:

0.1315 gave 0.3688 CO₂ and 0.0614 H₂O. C=76.48; H=5.19.

C₁₇H₁₄O₃ requires C=76.69; H=5.24 per cent.

4-Methoxy-1:3-dimethylantraquinone is soluble in acetic acid and sparingly so in alcohol or benzene. It is hydrolysed only with difficulty by sulphuric acid, and considerable decomposition ensues.

Condensations by Means of Boric Acid.

2'-Hydroxy-3'-methyl-2-benzoylbenzoic acid,

—This acid is prepared by heating a mixture of phthalic acid (or anhydride, 30 grams), *o*-cresol (30 grams), and boric acid (60 grams) to 170—180° until the yellow colour of the mixture commences to darken. The fusion is poured into a large quantity of water, boiled until free from *o*-cresol, and filtered hot. The residue consists of a mixture of *o*-cresolphthalein and hydroxymethylbenzoylbenzoic acid; the latter is extracted by repeatedly boiling the residue with water and calcium carbonate, filtering, and acidifying the filtrates with hydrochloric acid. The precipitated acid is collected and crystallised from acetic acid, from which it separates in plates melting at 196—197°:

0.1265 gave 0.3260 CO₂ and 0.0563 H₂O. C=70.28; H=4.94.

C₁₅H₁₂O₄ requires C=70.31; H=4.68 per cent.

2'-Hydroxy-3'-methyl-2-benzoylbenzoic acid dissolves in alcohol, ether, or acetic acid, but is only sparingly soluble in hot water. It dissolves in cold concentrated sulphuric acid forming a yellow solution which turns orange-red on heating owing to the production of

1-Hydroxy-2-methylantraquinone, C₆H₄ $\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}$ C₆H₂Me·OH.—This

substance is best prepared by dissolving the foregoing acid together with twice its weight of boric acid in concentrated sulphuric acid and carefully adding fuming sulphuric acid until the initial yellow colour changes to an intense red. The product is poured into water, the yellow precipitate filtered, washed with hot water, dried on porous

porcelain, and crystallised from acetic acid, from which it separates in fibrous needles melting at 184—185° :

0.1942 gave 0.5374 CO₂ and 0.0752 H₂O. C = 75.47 ; H = 4.30.

C₁₅H₁₀O₃ requires C = 75.63 ; H = 4.20 per cent.

1-Hydroxy-2-methylantraquinone dissolves in sulphuric acid with an orange-red colour. Its *potassium* salt is sparingly soluble in water, but readily so in alcohol with a bluish-red colour.

2'-Hydroxy-4'-methyl-2-benzoylbenzoic acid,

—This acid is prepared from *m*-cresol in the same manner as the corresponding acid from *o*-cresol. The dark red fusion is poured into water, boiled until free from *m*-cresol, and filtered. The residue, consisting of a mixture of the acid and the fluoran, is repeatedly extracted with boiling dilute aqueous sodium carbonate until no further precipitate appears on acidification. The united filtrates are acidified with hydrochloric acid, and the resulting white precipitate crystallised from methyl alcohol, from which it separates in prismatic plates melting at 210—211° :

0.1382 gave 0.3560 CO₂ and 0.0603 H₂O. C = 70.25 ; H = 4.84.

C₁₅H₁₂O₄ requires C = 70.31 ; H = 4.68 per cent.

2'-Hydroxy-4'-methyl-2-benzoylbenzoic acid dissolves in sulphuric acid with a yellow colour, which changes to an intense orange-red on heating.

4-Hydroxy-2-methylantraquinone, C₆H₄ < $\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix}$ > C₆H₂Me · OH, is prepared from the foregoing acid and purified in the same manner as 1-hydroxy-2-methylantraquinone :

0.1200 gave 0.3328 CO₂ and 0.0450 H₂O. C = 75.63 ; H = 4.16.

C₁₅H₁₀O₃ requires C = 75.63 ; H = 4.20 per cent.

This quinone melts at 178°, and is probably identical with that described by Römer and Link (*loc. cit.*). It is soluble in alcohol or acetic acid, from which it separates in yellow needles. Its *potassium* salt is sparingly soluble in water with a bluish-red colour.

3 : 6-Dimethylfluoran,* $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{O} \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{C}_6\text{H}_3\text{Me} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3\text{Me} \end{smallmatrix} \text{O}.$ —This substance remains after the removal of the acid just described from the fused mixture of phthalic acid, boric acid, and *m*-cresol. It crystallises from acetic acid or xylene in short prisms melting at 204—205° :

0.1384 gave 0.4076 CO₂ and 0.0642 H₂O. C = 80.32 ; H = 5.15.

C₂₂H₁₆O₃ requires C = 80.48 ; H = 4.87 per cent.

3 : 6-Dimethylfluoran dissolves in concentrated sulphuric acid yielding a yellow, fluorescent solution.

* For nomenclature, see Trans., 1902, **81**, 894.

2'-Hydroxy-5'-methyl-2-benzoylbenzoic acid,

is prepared from *p*-cresol and isolated from the fusion exactly like 2'-hydroxy-4'-methyl-2-benzoylbenzoic acid from *m*-cresol. It crystallises from methyl alcohol in plates melting at 194—195° :

0.1026 gave 0.2642 CO₂ and 0.0459 H₂O. C = 70.22 ; H = 4.97.

C₁₅H₁₂O₄ requires C = 70.31 ; H = 4.68 per cent.

2'-Hydroxy-5'-methyl-2-benzoylbenzoic acid dissolves in sulphuric acid, producing a yellow solution which, on the addition of boric acid and fuming sulphuric acid, changes to an orange-red owing to its condensation to 4-hydroxy-1-methylanthraquinone (p. 1633).

In the fusion of phthalic acid, boric acid, and *p*-cresol there is also formed 2 : 7-dimethylfluoran, which is isolated in the same way as the corresponding substance prepared from *m*-cresol. It melts at 250—252° (Drewsen, *Annalen*, 1882, **212**, 340, gives 246°) and dissolves in sulphuric acid forming a yellow solution more fluorescent than that produced by 3 : 6-dimethylfluoran.

2'-Hydroxy-3' : 5'-dimethyl-2-benzoylbenzoic acid,

is produced by heating a mixture of phthalic acid, boric acid, and *m*-4-xylenol to 180° for two hours. The acid is isolated from the fusion exactly like 2'-hydroxy-4'-methyl-2-benzoylbenzoic acid. It crystallises from methyl alcohol in plates melting at 165—166° :

0.1256 gave 0.3284 CO₂ and 0.0590 H₂O. C = 71.31 ; H = 5.22.

C₁₆H₁₄O₄ requires C = 71.11 ; H = 5.18 per cent.

2'-Hydroxy-3' : 5'-dimethyl-2-benzoylbenzoic acid dissolves in sulphuric acid with a yellow colour which changes to an orange-red on heating or on the addition of fuming sulphuric acid. On pouring the product into water, 4-hydroxy-1 : 3-dimethylanthraquinone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{HMe}_2 \cdot \text{OH}$, is precipitated. It crystallises from acetic acid in prismatic needles melting at 173—175° :

0.1420 gave 0.3986 CO₂ and 0.0622 H₂O. C = 76.55 ; H = 4.81.

C₁₆H₁₂O₃ requires C = 76.58 ; H = 4.76 per cent.

2 : 4 : 5 : 7-Tetramethylfluoran, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \quad \diagdown \\ \text{CO} \cdot \text{O} \end{smallmatrix} \text{C} \begin{smallmatrix} \diagdown \quad \diagup \\ \text{C}_6\text{H}_2\text{Me}_2 \\ \text{C}_6\text{H}_2\text{Me}_2 \end{smallmatrix} \text{O}$.—This tetra-

methylfluoran is also a product of the fusion of phthalic acid, boric acid, and *m*-4-xylenol, and remains as a brown powder after the extraction with sodium carbonate. It is obtained pure by crystallising from xylene with the aid of animal charcoal, when it separates in prisms melting at 247—249° :

0.1126 gave 0.3344 CO₂ and 0.0584 H₂O. C = 80.99; H = 5.76.

C₂₄H₂₀O₃ requires C = 80.90; H = 5.62 per cent.

The solution of this substance in concentrated sulphuric acid possesses an orange colour, but little fluorescence.

Hydroxy-o-cresolphthalein, $\text{HO} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \diagup \\ \text{CO} \cdot \text{O} \end{array} > \text{C} \begin{array}{c} \diagdown \\ \diagup \end{array} \begin{array}{c} \text{C}_6\text{H}_3\text{Me} \cdot \text{OH} \\ \text{C}_6\text{H}_3\text{Me} \cdot \text{OH} \end{array}$.—This sub-

stance was the only product which could be obtained from the fusion of 4-hydroxyphthalic acid, boric acid, and *o*-cresol by extraction with sodium carbonate. It crystallises from dilute acetic acid in white needles melting at 245—247°:

0.1290 gave 0.3435 CO₂ and 0.0577 H₂O. C = 72.62; H = 4.97.

C₂₂H₁₈O₅ requires C = 72.92; H = 4.94 per cent.

The substance dissolves in alkalis with a violet colour.

4(5): 2'-*Dihydroxy-4'-methyl-2-benzoylbenzoic acid*,

—This acid is prepared by heating a mixture of 4-hydroxyphthalic acid (30 grams), *m*-cresol (30 grams), and boric acid (60 grams) to 180° for two hours. The fused mass is poured into water, boiled, and filtered; the insoluble residue is then repeatedly boiled with water and calcium carbonate as long as the filtrate yields a precipitate on acidification. The united filtrates are acidified with hydrochloric acid, and the precipitate crystallised from acetic acid, from which it separates in plates melting at 228—229°:

0.1109 gave 0.2688 CO₂ and 0.0470 H₂O. C = 66.10; H = 4.70.

C₁₅H₁₂O₅ requires C = 66.17; H = 4.41 per cent.

4(5): 2'-*Dihydroxy-4'-methyl-2-benzoylbenzoic acid* is sparingly soluble in water. It dissolves in concentrated sulphuric acid with an orange colour which changes to red on heating or treating with fuming sulphuric acid, due to its condensation to

4:7(8)-*Dihydroxy-2-methylantraquinone*,

which separates from acetic acid as a dull, yellow powder melting at 284°:

0.1088 gave 0.2818 CO₂ and 0.0398 H₂O. C = 70.64; H = 4.06.

C₁₅H₁₀O₄ requires C = 70.86; H = 3.93 per cent.

4:7(8)-*Dihydroxy-2-methylantraquinone* is soluble in sodium carbonate or ammonia with an orange-red colour; it forms a dark red solution with sulphuric acid.

4'(5')-*Hydroxy-3:6-dimethylfluoran*, $\text{HO} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \diagup \\ \text{CO} \cdot \text{O} \end{array} > \text{C} \begin{array}{c} \diagdown \\ \diagup \end{array} \begin{array}{c} \text{C}_6\text{H}_3\text{Me} \\ \text{C}_6\text{H}_3\text{Me} \end{array} \text{O}.$ —

This substance remains with the excess of calcium carbonate after the extraction of the last-mentioned acid, and is obtained by repeated

extraction with boiling sodium carbonate and acidification of the alkaline extract. The precipitate is collected and crystallised from dilute acetic acid, from which it separates in plates melting at $320-325^{\circ}$:

0.1196 gave 0.3346 CO_2 and $0.0524 \text{ H}_2\text{O}$. $\text{C} = 76.30$; $\text{H} = 4.86$.

$\text{C}_{22}\text{H}_{16}\text{O}_4$ requires $\text{C} = 76.74$; $\text{H} = 4.65$ per cent.

4'(5')-Hydroxy-3:6-dimethylfluoran forms with sulphuric acid a yellow, but only slightly fluorescent, solution.

4(5):2'-Dihydroxy-5'-methylbenzoylbenzoic acid,

—This acid is prepared from *p*-cresol in the same manner as the corresponding acid from *m*-cresol. It separates from methyl alcohol as a white powder melting at 234° . It dissolves in concentrated sulphuric acid with a yellow colour which on the addition of fuming sulphuric acid becomes dark red, indicating condensation to

4:6(7)-Dihydroxy-1-methylantraquinone,

which separates from alcohol or acetic acid as a yellow powder melting at $244-246^{\circ}$:

0.1162 gave 0.3002 CO_2 and $0.0422 \text{ H}_2\text{O}$. $\text{C} = 70.46$; $\text{H} = 4.03$.

$\text{C}_{15}\text{H}_{10}\text{O}_4$ requires $\text{C} = 70.86$; $\text{H} = 3.93$ per cent.

This compound dissolves in sodium carbonate and ammonia yielding orange-red solutions.

4'(5')-Hydroxy-2:7-dimethylfluoran, $\text{HO}\cdot\text{C}_6\text{H}_3\begin{matrix} \diagup \quad \diagdown \\ \text{CO}\cdot\text{O} \end{matrix}\text{C}\begin{matrix} \diagdown \quad \diagup \\ \text{C}_6\text{H}_3\text{Me} \end{matrix}\text{C}\begin{matrix} \diagup \quad \diagdown \\ \text{C}_6\text{H}_3\text{Me} \end{matrix}\text{O}\cdot$ —

This hydroxydimethylfluoran, prepared from *p*-cresol, is isolated and purified in the same way as the corresponding one from *m*-cresol. It crystallises in minute needles melting at 284° :

0.1134 gave 0.3186 CO_2 and $0.0472 \text{ H}_2\text{O}$. $\text{C} = 76.62$; $\text{H} = 4.62$.

$\text{C}_{22}\text{H}_{16}\text{O}_4$ requires $\text{C} = 76.74$; $\text{H} = 4.65$ per cent.

It dissolves in cold aqueous sodium hydroxide and in hot sodium carbonate. Its solution in concentrated sulphuric acid is yellow and fluorescent, but much less so than 2:7-dimethylfluoran.

4(5):2'-Dihydroxy-3':5'-dimethylbenzoylbenzoic acid,

—This acid is prepared from *m*-4-xyleneol by the same process as that described for the corresponding acid from *m*-cresol. It crystallises from methyl alcohol in short prisms melting indefinitely at about 230° :

0.1303 gave 0.3203 CO_2 and $0.0578 \text{ H}_2\text{O}$. $\text{C} = 67.04$; $\text{H} = 4.93$.

$\text{C}_{16}\text{H}_{14}\text{O}_5$ requires $\text{C} = 67.13$; $\text{H} = 4.89$ per cent.

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The compound dissolves in sulphuric acid with a yellow colour, which changes to a bluish-red on heating the solution.

4 : 6(7)-*Dihydroxy-1 : 3-dimethylantraquinone*,

—This quinone is prepared from the preceding acid in the usual way by treatment with fuming sulphuric acid. It was also found that the substance had been produced directly in the boric acid fusion, and was obtained in the sodium carbonate extract instead of the anticipated hydroxytetramethylfluoran. It crystallises from acetic acid in needles melting at 270° :

0.1395 gave 0.3668 CO_2 and 0.0590 H_2O . $\text{C} = 71.71$; $\text{H} = 4.69$.

$\text{C}_{16}\text{H}_{12}\text{O}_4$ requires $\text{C} = 71.64$; $\text{H} = 4.48$ per cent.

The compound dissolves in concentrated sulphuric acid with a bluish-red, and in sodium carbonate and ammonia with an orange-red, colour.

Methoxymethyl-β-benzoylpropionic acid,

—This acid is prepared by dissolving *m*-cresol methyl ether (30 grams) in a large quantity of carbon disulphide, adding succinic anhydride (25 grams) and aluminium chloride (10 grams), and heating the mixture on the water-bath in a reflux apparatus for six hours. The carbon disulphide is then decanted from the hard mass, which is disintegrated by the addition of ice and hydrochloric acid, and volatile impurities removed by steam. The residue is filtered, dissolved in sodium carbonate, precipitated with hydrochloric acid, and finally crystallised from water, from which it separates in colourless prisms melting at 131 — 132° :

0.1312 gave 0.3086 CO_2 and 0.0754 H_2O . $\text{C} = 64.15$; $\text{H} = 6.38$.

$\text{C}_{12}\text{H}_{14}\text{O}_4$ requires $\text{C} = 64.86$; $\text{H} = 6.30$ per cent.

Methoxymethyl-β-benzoylpropionic acid is soluble in alcohol, acetic acid or benzene. It yields a greenish-brown solution with concentrated sulphuric acid.

Methoxy-3-methyl-β-benzoylacrylic acid,

—This acid is prepared from *o*-cresol methyl ether and maleic anhydride in exactly the same manner as the foregoing acid. It separates from benzene as a yellow powder melting at 113° :

0.1970 gave 0.4711 CO_2 and 0.0977 H_2O . $\text{C} = 65.23$; $\text{H} = 5.51$.

$\text{C}_{16}\text{H}_{12}\text{O}_4$ requires $\text{C} = 65.45$; $\text{H} = 5.45$ per cent.

The acid is very sparingly soluble in water, but readily so in alcohol, benzene, or acetic acid. It dissolves in sulphuric acid with a greenish-brown colour.

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