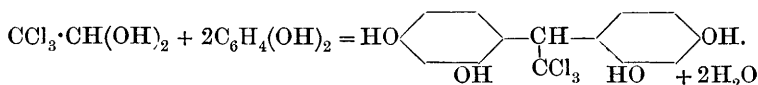


XCIX.—*The Condensation of Chloral with Resorcinol.*  
(*Second Communication.*)

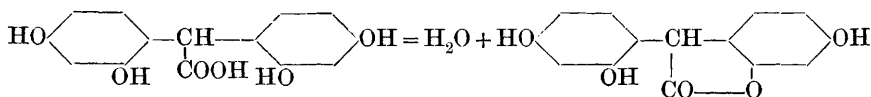
By J. T. HEWITT, M.A., D.Sc., Ph.D., and FRANK G. POPE.

ABOUT a year ago we laid a paper before the Society (Trans., 1896, 69, 1265) in which we gave the results obtained in studying the condensation of chloral hydrate and resorcinol when warmed together in dilute aqueous solution in presence of acid sodium sulphate. Our results differed from those of H. Causse (*Bull. Soc. Chim.*, 1890, [iii], 3, 861), in that, whilst we found that the formula of the substance produced was  $C_{14}H_{10}O_5$ , and that this was unchanged even after heating for 8 hours at a temperature of  $190^{\circ}$ — $200^{\circ}$ , yet on warming with acetic anhydride, a product was obtained the analysis of which pointed to the formula  $C_{14}H_7O_5(C_2H_3O)_3$ , and not  $C_{14}H_{10}O_6(C_2H_3O)_2$ , as obtained by Causse. We were, therefore, led to consider the condensation as taking place in an analogous manner to the ordinary course followed by aldehydes in their reaction with resorcinol or alkylated meta-amidophenols.



The next step would be the hydrolysis of the trichlormethyl- to a carboxyl-group, lactone formation then taking place between this

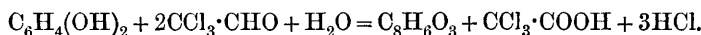
carboxyl-group and one of the orthohydroxyl-groups according to the equation



Such an explanation would agree well, not only with the results obtained by the combustion of the substance and its acetyl derivative, and with the analysis of the barium salt, which one would expect to possess the composition  $\text{Ba}(\text{C}_{14}\text{H}_{11}\text{O}_6)_2$  if the substance having the formula  $\text{C}_{14}\text{H}_{10}\text{O}_5$  be a lactone, but would also come into line with the many condensations between aldehydes and resorcinol which have been studied by other chemists.

One fact alone is difficult to reconcile with our supposition. The salts of the acid  $\text{C}_{14}\text{H}_{12}\text{O}_6$  are probably colourless when pure, but when the lactone itself is first dissolved in an alkali, an intense purple coloration is produced, very similar to that observed when phenolphthalein is dissolved in an alkali. This strongly coloured solution contains a salt of the lactone, since the latter is immediately precipitated by the addition of acids. Despite the brilliant colour of the alkaline solution, one sees no feasible way in which one can assign to the dissolved salt a quinonoid constitution.

In the course of a conversation concerning this peculiar behaviour, Professor von Kostanecki pointed out to one of us that the condensation of chloral with resorcinol had already been studied by Michael and Comey (*Amer. Chem. Journ.*, 1883—1884, 5, 350), who came to the conclusion that the reaction took place according to the following equation :



These authors, from the analysis of the acetate and benzoate, concluded that the compound contained two hydroxyl groups.

In 1887, Claisen (*Annalen*, 1887, 237, 263) drew attention to Michael's paper, pointing out that, having regard to the work of von Baeyer and his pupils, it seemed strange that one molecule of an aldehyde should react with only one and not with two molecules of resorcinol.

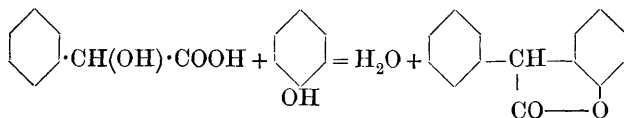
Shortly afterwards, Michael and J. P. Ryder published a further paper on the condensation of aldehydes with phenols (*Amer. Chem. Journ.*, 1887, 9, 134), in which the reaction between chloral hydrate and orcinol when heated together in a reflux apparatus in aqueous solution is described. The authors give the much greater stability of the product formed as a reason for the choice of orcinol in place of the lower homologue.

The result of their work was to attribute the formula  $\text{C}_{23}\text{H}_{24}\text{O}_8$  to the nearly colourless compound so obtained, whilst the acetyl derivative

was formulated as  $C_{35}H_{34}O_{13}$ . That is to say, the condensation was supposed to take place with elimination of hydrogen chloride, the whole six hydroxyl groups of the three orcinol molecules remaining intact. Moreover, the  $-CH(OH)$  grouping was supposed to remain unchanged after the condensation, although on acetylation it was dehydrated to  $-CHO$ .

Without further touching on the orcinol condensation, it may be pointed out that if resorcinol and chloral hydrate are supposed to condense in a similar proportion of three molecules of the former to one of the latter, Michael's own analyses will not agree with the formulæ of the substances obtained.

Should, however, our explanation of the condensation be correct, the substance we obtained must stand in a near relationship to the ortho-hydroxydiphenylacetic lactone obtained by Bistrzycki and Flatau (*Ber.*, 1895, 28, 989, and 1897, 30, 124) by the condensation of mandelic acid and phenol in presence of concentrated sulphuric acid according to the equation



Professor Bistrzycki has now found that mandelic acid and resorcinol similarly condense, giving a pair of isomeric lactones, the one which

probably possesses the formula  $\text{C}_6\text{H}_5\text{CH}(\text{CO}-\text{O}-\text{C}_6\text{H}_3(\text{OH})_2)_2$  dissolving in al-

kalis with a not very intense orange colour, although itself a colourless substance.\* This fact, taken in conjunction with the evidence we now bring forward, leaves in our minds scarcely any doubt that we have ascribed to the substance its correct constitution.

The condensation of resorcinol and chloral hydrate is not very satisfactory as regards yield. The first crop of substance is always fairly colourless after washing with cold water with the aid of a filter pump, but succeeding quantities are generally darker in colour; it is therefore advisable, when a fair quantity of the substance has been formed, to cool the liquid, filter off the substance, wash this with cold water, the washings being added to the filtrate, and then to proceed with the warming process. Since a certain amount of tarry matter is always obtained in the later stages, it is most advisable to carry out

<sup>1</sup> Private communication. I must express my best thanks to Professor Bistrzycki for his kindness in sending me a small specimen of the substance in order to see the coloured solution in alkali for myself.—J. T. HEWITT.

the above precaution, otherwise the whole quantity may be obtained in a condition very troublesome to purify.

In order to settle the question of rational formula, Mr. F. Dixon, B.Sc., determined the molecular weight by the lowering of the freezing point of a solution in phenol.

Theory for.			Found.
$\text{C}_8\text{H}_6\text{O}_3$	$\text{C}_{14}\text{H}_{10}\text{O}_5$	$\text{C}_{20}\text{H}_{18}\text{O}_8$	
150	258	386	232.

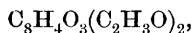
Michael noted that the lactone, when dissolved in concentrated sulphuric acid, acquired a fine blue colour when exposed to the air. We find that very little coloration is produced in the cold, even when the substance is industriously stirred with strong sulphuric acid on a watch-glass. This may be due to the substance not being thoroughly wetted, for if the contents of the watch glass be gently warmed, all goes into solution with a splendid blue shade which remains after the solution has cooled. If the cold concentrated sulphuric acid solution be diluted with water, the colour is nearly entirely discharged, a feeble, reddish shade, due to limited oxidation, alone remaining.

*Acetyl Derivative.*—In our previous paper, we gave a preparation and analysis of the acetate; we now find that it is better not to heat for so long a time as we had previously done. A beautiful product is obtained by gently boiling one part of the lactone with ten parts of acetic anhydride in a reflux apparatus. Whereas the lactone is very far from being entirely dissolved by this weight of the anhydride, the acetyl derivative is entirely soluble. At the end of one hour, solution being by that time completely effected, the mixture is poured into a large excess of water and the acetate precipitated in a colourless condition.

The precipitate soon becomes granular on stirring, and after collecting and recrystallising from glacial acetic acid, is obtained in glittering, rectangular plates. When examined under the microscope ( $\times 420$ ), the substance proved to be perfectly homogeneous. The corrected melting point was found at  $160.5^\circ$ ; Michael's acetate melted at  $159^\circ$ . The new preparation of the acetate was analysed, the result being in good agreement with that previously obtained.

Theory for $\text{C}_{14}\text{H}_7\text{O}_5(\text{C}_2\text{H}_3\text{O})_3$ .	C = 62.50 ; H = 4.17.
Found .....	C = 62.52 ; H = 4.19.
Found previously.....	C = 62.22 ; H = 4.31.
Michael and Comey's results.	C = 61.71, 61.70, 61.20 ; H = 4.32, 4.67, 4.51.

It may be added that Michael's formula for the acetate,



requires C = 61.54 ; H = 4.27.

The acetate dissolves in concentrated sulphuric acid with a greenish shade, the green colour becoming very intense and rather dark on warming. On dilution with water, the solution turns brownish-yellow and finally yellow; this change is possibly due to partial hydrolysis and oxidation.

When the acetate is moistened with 50 per cent. solution of potassium hydroxide, no immediate change is produced; after a very short time, the mixture becomes intensely pink, the colour being practically discharged on warming, complete hydrolysis taking place.

*Benzoyl Derivative.*—We conducted benzoylation experiments under various conditions, such as heating with excess of benzoyl chloride, trying the Schotten-Baumann reaction with alkaline solutions, both freshly prepared, and, therefore, containing lactone, and boiled, and so containing the sodium salt of the acid  $C_{14}H_{12}O_6$ , as well as benzoylating in pyridine solution.

The method described by Michael is to be preferred for the purpose of preparation, namely, heating the lactone with about five times its weight of the acid chloride at  $120^\circ$  until the disengagement of hydrogen chloride has ceased.

The product is then boiled out with water, and repeatedly recrystallised from alcohol. Michael describes the benzoyl compound as small crystals having a faintly pinkish tint, and melting at  $165^\circ$ . We obtained our crystals with a somewhat yellowish shade; they consisted of radiating aggregates of prisms. It seems very probable that the substance is, like the acetate, quite colourless when pure; the preparation of the substance seems to be attended in any case with the production of a certain amount of tarry bye-product rather difficult to remove.

Michael formulated the substance as  $C_8H_4O_3(C_7H_5O)_2$ ; we prefer to regard it as possessing the formula,  $C_{14}H_7O_5(C_7H_5O)_3$ . The percentage compositions required by these two formulæ differ very slightly.

Theory for $C_8H_4O_3(C_7H_5O)_2$ ...	C = 73·74 ; H = 3·91.
"    " $C_{14}H_7O_5(C_7H_5O)_3$ ...	C = 73·68 ; H = 3·86.
Found.....	C = 72·83, 73·11 ; H = 3·99, 4·67.
Found by Michael and Comey...	C = 73·62 ; H = 4·47.

The benzoate dissolves in concentrated sulphuric acid with an indigo shade, which becomes a purer blue on warming.

The same benzoate is obtained by dissolving the lactone in pyridine and shaking the solution with benzoyl chloride. The addition of the latter warms the solution slightly, and, on adding water, the benzoate comes down in a tarry condition. To effect its isolation, hydrochloric acid is added in excess to combine with the pyridine and the benzoate

extracted with chloroform. By careful addition of petroleum spirit to the chloroform solution, a dark-coloured impurity may be fractionally precipitated, and the liquid, on spontaneous evaporation, then gives nearly colourless crystals of the benzoate.

When a fresh solution of the lactone in caustic soda is agitated with benzoyl chloride, apparently the same benzoate is obtained. We hoped to get other results, by dissolving the lactone in alkali, warming so as to open the lactone ring, and then agitating with benzoyl chloride. It was expected that we should obtain a tetra-benzoylated tetrahydroxydiphenylacetic acid of the formula  $\text{COOH} \cdot \text{CH}[\text{C}_6\text{H}_5(\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_5)_2]_2$ , which by oxidation in alkaline solution might be expected to yield tetrabenzoyltetrahydroxybenzophenone. The corresponding tetrahydroxybenzophenone should pass over into 3:6-dihydroxyxanthone on heating. We were, however, disappointed in this reaction. On agitating the alkaline solution with benzoyl chloride, a precipitate was immediately obtained, consisting for the most part of the tribenzoylated lactone. The lactonisation thus induced by benzoylation may perhaps be conditioned by the spacial relationships within the molecule.

Further evidence of the presence of three hydroxyl groups in the molecule  $\text{C}_{14}\text{H}_{10}\text{O}_5$  is afforded by the behaviour of the absolute alcoholic solution of the substance with sodium ethylate. On adding the latter to the former, a most intense and very beautiful violet-blue coloration is produced which is replaced by a red colour as the addition of the sodium ethylate is continued. The blue compound is apparently formed provided the amount of sodium added does not exceed two atoms per molecule of lactone. The red compound contains three atoms of sodium. This was proved by adding a considerable excess of sodium ethylate to a solution of the lactone in absolute alcohol. The crystalline precipitate so obtained was collected with the aid of the filter pump, washed first with absolute alcohol and then with ether, and dried on a porous tile in a vacuum over sulphuric acid. The analysis gave the following result:

Calculated for $\text{C}_{14}\text{H}_7\text{O}_5\text{Na}_3$ .....	Na = 21.30
Found.....	Na = 22.10

Attempts at replacement of this sodium by ethyl gave very unsatisfactory results.

We previously stated that the solution obtained by boiling the lactone with bases contained salts derived from tetrahydroxydiphenylacetic acid. In support of this statement, we brought forward the analysis of the barium salt, to this we may now add the preparation and analysis of zinc tetrahydroxydiphenylacetate.

*Zinc Salt.*—This was prepared by boiling zinc carbonate and the lactone with water until evolution of carbon dioxide had entirely

ceased. The solution was then filtered and evaporated in a vacuum desiccator over concentrated sulphuric acid. The crystals deposited were externally darkly coloured from the oxidation which had taken place during the evaporation owing to a small quantity of air being left in the desiccator. After drying, they were, however, found to give a nearly colourless powder, so that the oxidation can only have been superficial. After carefully drying to constant weight at  $105^{\circ}$ , zinc was estimated in the salt.

Calculated for  $\text{Zn}(\text{C}_{14}\text{H}_{11}\text{O}_6)_2$ .....  $\text{Zn} = 10\cdot57$

Found .....  $\text{Zn} = 10\cdot64$ .

As the result of repeating our work, we consider that we have definitely settled the composition of the compounds concerned, with regard to their constitution scarcely any other formulation appears to us very tenable.

EAST LONDON TECHNICAL COLLEGE,

*July, 1897*

---