ASPECTS OF THE

RESORCINOL - FORMALDEHYDE

CONDENSATION.

-by-

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The work described in this dissertation is, unless otherwise stated, original.

A SUMMARY OF

'ASPECTS OF THE RESORCINOL-FORMALDEHYDE CONDENSATION'.

An attempt was made to produce a β - or γ-resorcinyl alcohol from disubstituted resorcinols. To accomplish this 3,5-dibromo-β-resorcylic acid was reacted with lithium aluminium hydride, a mild reducing agent, in an attempt to reduce the acid group to the alcohol group. This disubstituted resorcinol was recovered unchanged. 3,5-dibromo-β-resorcylaldehyde was reduced by lithium aluminium hydride, but, instead of the alcohol forming, resinification took place. 2-methyl-4-ethylresorcinol and 4,6-diethylresorcinol were reacted with formaldehyde under alkaline and acidic conditions. In each case a resin formed.

The above experiments indicated that condensation took place in the meta position of the resorcinol molecule. Trimethylresorcinol was therefore reacted with formaldehyde under alkaline conditions, resulting in a small quantity of the alcohol derivative.

A better yield of the alcohol derivative was obtained by the hydrolysis of the chloromethyl derivative. In pursuing this line, a series of new compounds and their derivatives were prepared.

The condensation of the alcohol derivative with trimethylresorcinol and also with resorcinol was investigated.

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I. HISTORICAL AND INDUSTRIAL BACKGROUND

In these days of industrialisation, manufacturers are not slow in availing themselves of any new and useful product of the laboratory, and, in this respect, plastics are no exception.

In 1909, Baekeland made his two brilliant proposals to overcome the difficulty previously experienced in moulding the phenoplasts. These were the use of a filler, such as wood flour, to overcome brittleness, and the use of heat and pressure during the moulding which shortened the moulding time and prevented porosity (1). Since then the expansion of the phenoplast industry has been so great that recent surveys (2) have indicated that the present annual output in the United States of 334,000,000 pounds phenol will have to be doubled to meet demands.

Added to this, there are many other fields of human activity which call for the development and improvement of these substances, apart from the commercial aspect.

Since the phenol compounds form the basis of an important section of plastics, it is logical for the chemist to centre his research work on those compounds when endeavouring to satisfy the insistent demands for

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better and more adaptable plastic materials, and for the elucidation of the chemical mechanism by which they are formed. The theoretical investigations of the phenoplasts have not kept pace with the industrial development.

The applications of phenol-formaldehyde resins are very numerous but they can be divided briefly into five main groups, namely, moulding powders, protective coatings, adhesives, cast resins and ion exchange resins (3).

Whereas phenol-formaldehyde resins find wide use in industry, resorcinol-formaldehyde resins are, in comparison, very seldom used. The reason for this is that phenol is cheaper than resorcinol. However, in practice, resorcinol, like phenol, reacts with formaldehyde to form a resin, but the curing time is less and the curing temperature is lower in the case of resorcinol.

In heat-reactive phenol-formaldehyde resins, the inclusion of resorcinol in the formulation can reduce the curing time or curing temperature or both.

In the adhesive field, a pure resorcinol-formaldehyde adhesive will cure at room temperature in 8 to 10 hours without catalysts injurious to cellulose fibres. At an elevated temperature, such as 120° F., the same resorcinol adhesive will cure in about one hour.

Straight phenolic adhesives, unless rendered strongly acidic, are not reactive at these temperatures and must

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be heated to 200° F. or higher. Cold setting neutral gap filling glues have been prepared from resorcinol-formaldehyde (4,5,6,7,8,9,) which can be used for gluing wood. The join withstands boiling water, and, when tension is applied, the wood will break before the joint. Other industrial applications of the resorcinol-formaldehyde resins are in the improvement of the wet strength of paper (4,5) and in the manufacture of laminar materials (10) and new resins (11,12).

When one considers the number of uses to which phenol-formaldehyde resins can be applied in comparison with resorcinol-formaldehyde resins, it becomes apparent why so much attention has been devoted to the former and so little to the latter. A vast amount of work has been done to elucidate the phenol-formaldehyde condensation and a well established theory has been constructed around it.

The present research work is directed towards the elucidation of the resorcinol-formaldehyde condensation on the same lines as for the phenol-formaldehyde.

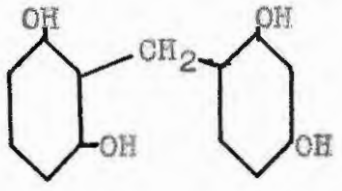
Resorcinol, having two ortho-para directing hydroxy groups, is consequently doubly activated in the positions ortho and para to those groups and reacts rapidly and

/easily....

easily with formaldehyde. This accounts for the fact that resorcinol is more reactive towards formaldehyde than phenol. There exists, however, a fundamental difference in behaviour between phenol and resorcinol in that, whilst both on treatment with formaldehyde resinify at room temperature under acidic conditions, only resorcinol does so under neutral or alkaline conditions.

Briefly the history of research work on the resorcinol-formaldehyde condensation is as follows:

In 1872 Baeyer (13) condensed resorcinol with various aldehydes. When the aldehyde was relatively inactive, crystalline compounds could be obtained. With resorcinol and acetaldehyde or formaldehyde, resinous products resulted. Caro (14), in 1892, condensed an excess of resorcinol with formaldehyde in the presence of dilute hydrochloric acid; the product obtained was identified as tetrahydroxydiphenylmethane

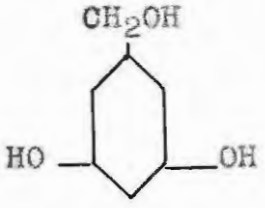


Möhlan and Koch (15) confirmed Caro's results. In 1924, Zamparo (16) reported on the ease with which resorcinol and formaldehyde form condensation products

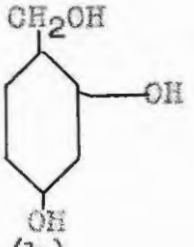
/in.....

in the cold.

Boehm and Parlasia (17) prepared methylol derivatives of resorcinol by reduction of the corresponding dicarbomethoxy aldehydes. The compound (a) was stable and not sensitive to acids, while compound (b) could not be prepared in a pure form, but always occurred as a resin.



(a)



(b)

Boehm and Parlasia also stated that the product obtained by Sen and Sarkar (18) through condensation of resorcinol with formaldehyde and designated β-resorcinyl alcohol was misbranded, being, in fact, a high molecular weight condensation product of unknown structure.

Raff and Silverman (19) claim that, in the condensation of resorcinol with formaldehyde, intermediate phenol alcohols, and resols are, if at all, stable only at temperatures of 5°C. or lower.

The formation of colloidal resin suspensions from formaldehyde and resorcinol and their flocculation by ions was described by Engeldinger (20) in 1936. Further kinetic study of the resorcinol-formaldehyde reaction

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was reported by Dubrisay and Papault (21) in 1942 and 1945. These authors condensed resorcinol with formaldehyde in the presence of sodium hydroxide, and determined the viscosity and the amount of free resorcinol in the solution. The results were considered to be in agreement with a reaction mechanism involving the formation of o-and p-phenol alcohols, their combination to substituted dihydroxydiphenylmethanes, and the condensation of these compounds to networks. Sprung and Gladstone (22) reported that the reaction of o-methylol phenol (saligenin) is of second order. Little and Pepper (23) found that the gel time of the resorcinol-formaldehyde condensation varied with pH in such a way that, when one was plotted against the other, the curve showed a maximum at pH 3-4 and a minimum at about pH 7 - 7.5. According to Granger (24), the minimum is due to Cannizzaro's reaction. Little and Pepper explain the maximum by plotting $\log_{10}$gel time and obtain a graph of two straight lines intersecting at pH 3-4 on extrapolation. They point out that the two linear portions of the curve indicate two reaction mechanisms, one catalysed by hydrogen ions and the other by hydroxyl ions. They suggest that the basic reaction between formaldehyde ano resorcinol to form firstly a phenolic alcohol and then a disubstituted

/methane.....

methane may be catalysed by either hydrogen ions or hydroxyl ions. Rhodes (25) connects the technical development of the resorcinol adhesives to the increasing knowledge of the effect of pH on their reactivity. Raff and Silvermann (19) found the uncatalysed resorcinol-formaldehyde reaction to be of the first order for different resorcinol-formaldehyde ratios and under changing temperature conditions.

In 1951 Ryding (26) attempted to prepare aβ - or γ-resorcinyl alcohol. Prior to his research work, no such methylol derivatives had been formed, and, in all cases, a resin had been produced. To restrict the condensation, Ryding used resorcinol compounds in which two of the three ortho and para positions were blocked by substituents, leaving one at which, he hoped, condensation would take place.

The three main methods of preparing the resorcinyl alcohol employed by him were:

(1) To react disubstituted resorcinol compounds with formaldehyde.

(2) To hydrolyse the chloromethyl derivative of a disubstituted resorcinol.

(3) To reduce a resorcinyl aldehyde to a resorcinyl alcohol.

His results were as follows:

/ (1).....

(1) (a) 4,6-Dibromoresorcinol was reacted with 40% formaldehyde under various conditions of temperature, solvent and catalyst. In each case a resin was produced. He found that formalin and sodium hydroxide removed the bromine atoms.

(b) He attempted to condense 5-nitro-β- resorcylic acid with formalin, using both acid and alkali as catalysts at various temperatures, but failed. The presence of nitro and carboxyl groups deactivated the benzene nucleus, thus preventing reaction from taking place.

(c) With 2,4-diniatroresorcinol, the result was the same as for 1 (b).

(d) 4,6-Diallylresorcinol, when reacted with formalin, yielded a small quantity of brownish amorphous material which he assumed to be a resin.

(e) On reacting 3,5-dibromo-β-resorcylic acid and formalin according to the Manasse reaction, he obtained a compound which was probably 2,3,4,5-tetrahydroxy-benzoic acid.

2. (a) The chloromethylation product of 4,6-diallyl-resorcinol could not be fully investigated because of shortage of reagents, but he suspected that 2-chloro-methyl-4,6,-diallylresorcinol had been formed. His

/attempted.....

attempted hydrolysis with silver oxide failed.

(b) Chloromethylation of Gallic acid yielded 2,2'-3,3'-4,4'-hexahydroxy-6,6'-dicarboxydiphenylmethane.

(c) On chloromethylation, 3,5-dibromo-β-resorcylic acid gave a small amount of 4,4'-6,6'-tetrabromo-3,3'-5,5'-tetracarboxydiphenylmethane. Condensation had taken place.

3. (a) Using platinum oxide as catalyst, 3,5-dibromo-β-resorcylaldehyde was catalytically hydrogenated to give a resin.

(b) Shortage of reagents hampered his work on diallylresorcinol but there was definite evidence that some 2,6-dihydroxy-3,5-diallylbenzaldehyde was prepared by the Gattermann reaction on diallylresorcinol. The attempt to reduce the aldehyde by hydrogenation yielded a new aldehyde, thought to be 2,6-dihydroxy-3,5-dipropylbenzaldehyde.

In conclusion, Ryding stated that, if the phenolic alcohol were in fact formed, it was extremely reactive and condensed rapidly with any free positions in the ring of the neighbouring molecule. If the resorcinol molecule was highly substituted, the deactivating effects of the substituent groups would have to be considered, particularly in the case of nitro groups.

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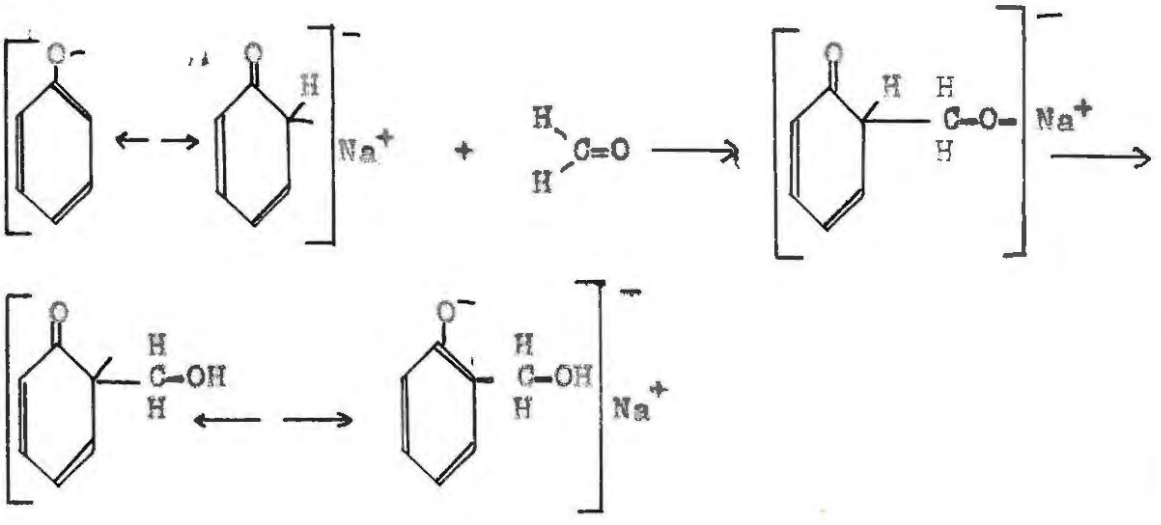
He suggested that a suitable line of attack might be the conversion of diallyl resorcinol to dipropyl-resorcinol, the aldehyde of which might be reduced with lithium aluminium hydride to the required alcohol.

II. STRUCTURE OF PHENOL FORMALDEHYDE RESINS

Phenol and formaldehyde can react to form three dimensional macromolecules when catalysed either by an alkali or an acid. The chemistry of the alkali catalysed condensation is markedly different from the acid catalysed reaction.

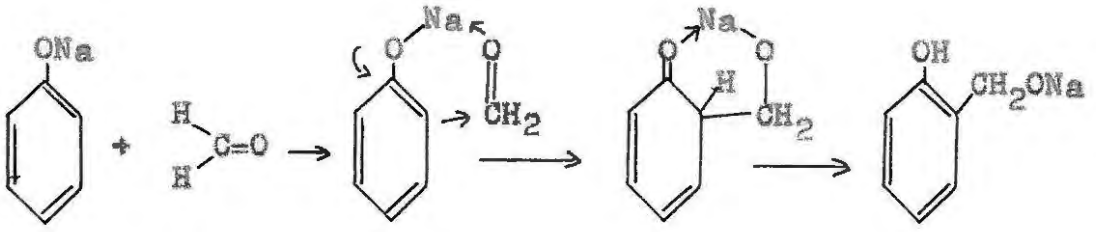
CONDENSATION IN ALKALINE SOLUTION

It is generally accepted that the initial reaction of formaldehyde with phenol yields a phenol alcohol. Hultzsch (27) and Ziegler (28) suggested that the alcohol might form through an aldol condensation as follows:



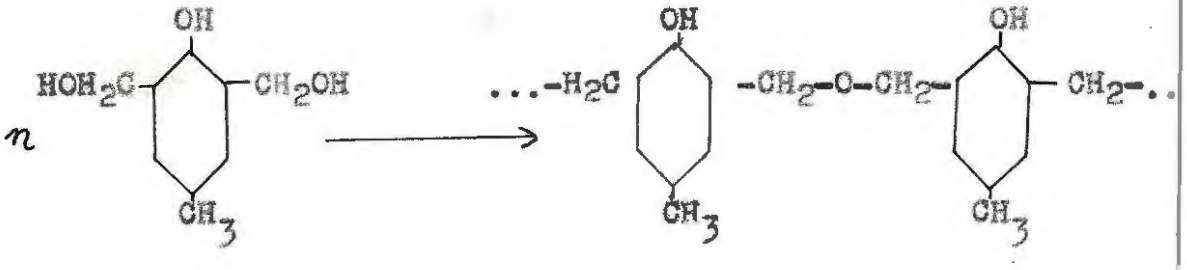
Basically the reaction consists of the removal of a proton from phenol by the alkali.

Price (29) visualised that phenol reacts with formaldehyde to form a chelate ring. Intramolecular rearramgement gives the phenol alcoholate:



The alcohol formation can take place at all three ortho and para positions and further reaction yields insoluble and infusible resins. To study the curing reactions therefore, phenols with one or two ortho and para positions blocked, were used. Even though substituents in the phenolic nucleus affect the curing reaction, it was only through setting up model reactions that knowledge of the curing mechanism could be gained.

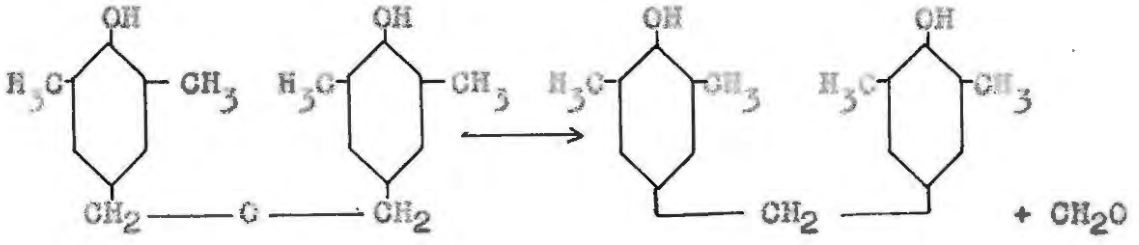
The principal thermal reaction in the early stages of curing, at temperatures 100 - 140°C., appears to be the formation of dibenzyl ether linkages between phenolic nuclei. The dialcohol from p-cresol forms long chain ethers on heating:



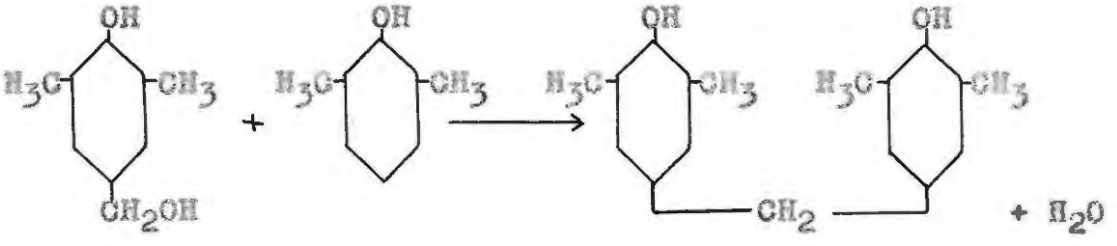
In many cases of highly substituted phenols, dibenzyl ethers form the largest single product isolated from the cured reaction mass.

Ether formation is retarded by the increase in temperature or by the presence of alkali (30), when diphenylmethane compounds form.

On further heating, particularly at temperatures higher than are needed to form the ether, the latter may split off formaldehyde and give a diphenylmethane:



When a phenol alcohol is heated to 140 - 155°C., formaldehyde splits off with the regeneration of phenol, which condenses with unchanged alcohol to form diphenylmethane and water.

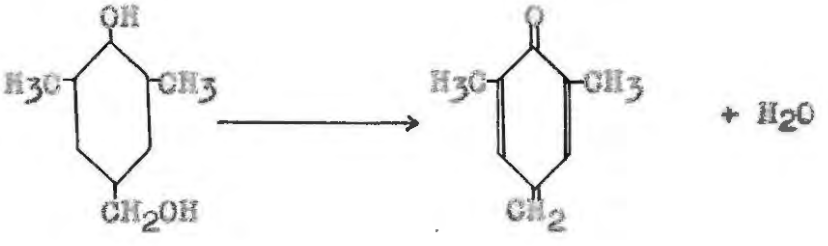


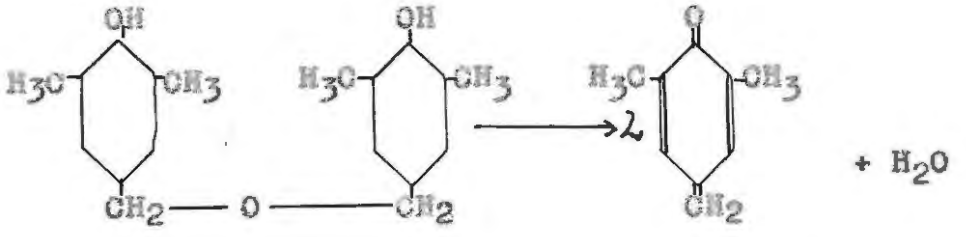
For phenol with three reactive positions, the intermediates are mono-, di- and trialcohols. These

/compounds.....

compounds react quickly with one another under continuous heating while water as well as formaldehyde split off forming ether linkages between the benzene nuclei.

In addition to the condensation reactions outlined above, there is evidence that at least part of the resin may be formed by polymerisation. Investigators have shown that the curing reaction was catalysed by the treatment of formaldehyde with ozone, whereby peroxides might be formed. The latter would evidently be catalysts for the polymerisation reaction and would be expected to have no effect on condensation. Dimers and trimers of methylenequinone have been identified from the reaction products from the curing of highly substituted phenols. Methylenequinone, the unstable monomer, may be formed at temperatures around 200°C. from the phenol alcohol or the dihydroxybenzyl ether, with the splitting off of water.





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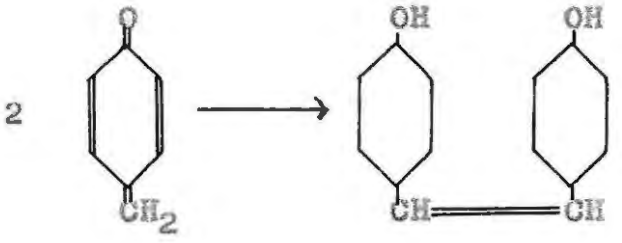
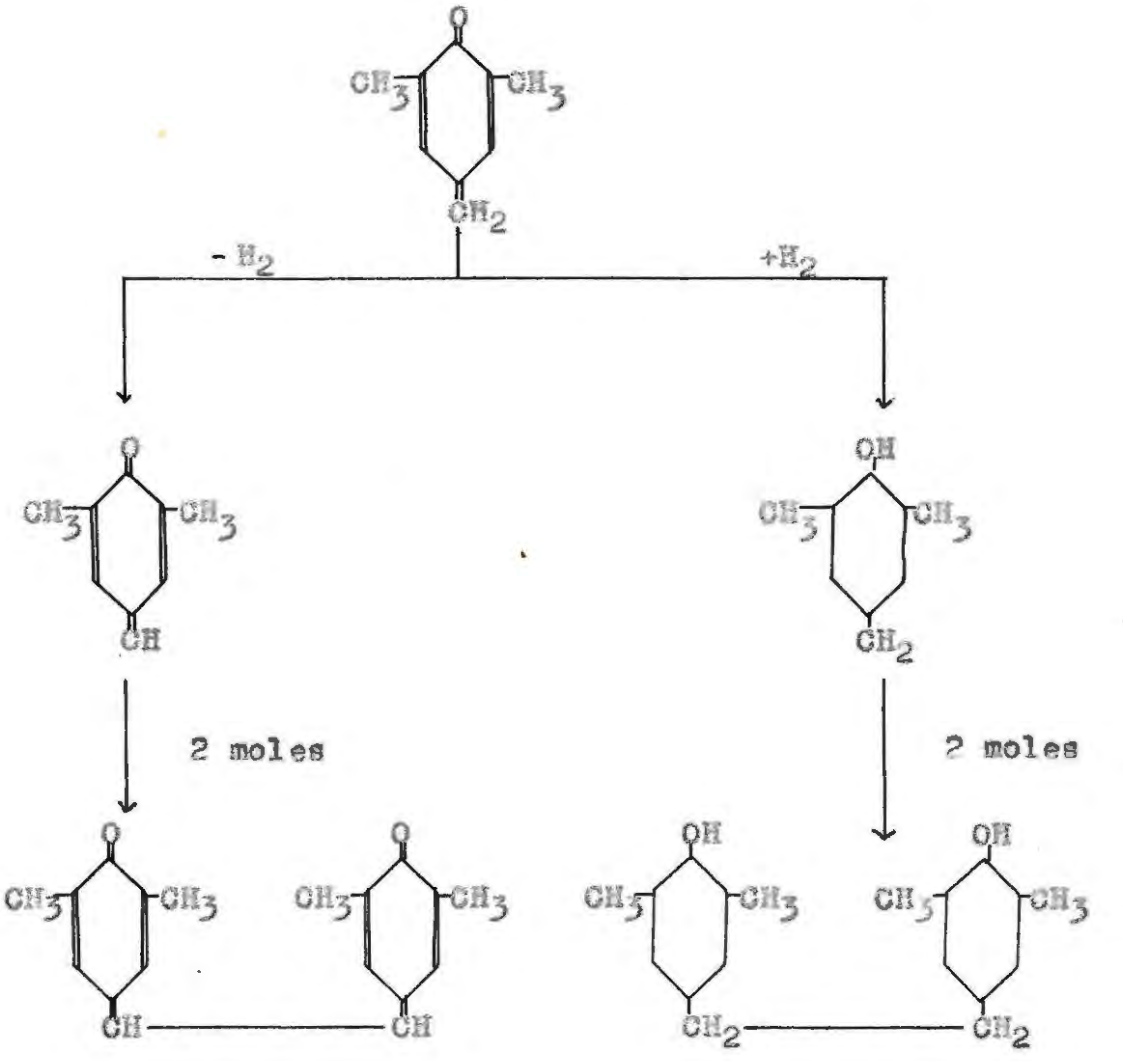
The ortho compound is also formed when the methylol group is in the ortho position.

Methylenequinone may dimerize to give dihydroxy-stilbene.



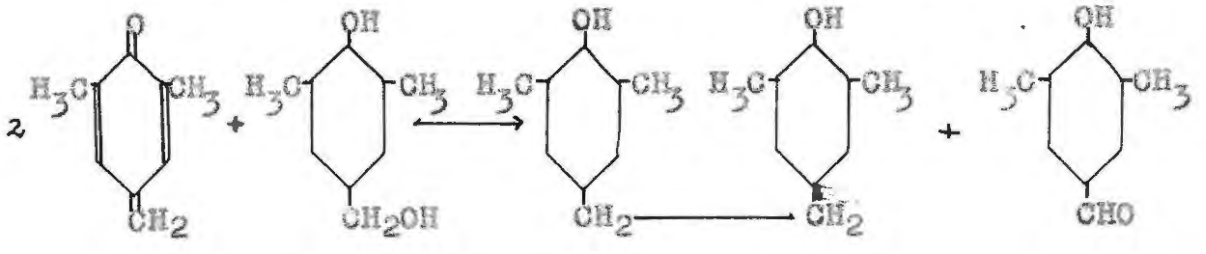
It may also undergo a direct disproportionation, while in an unstable state, and yield radicals which become stabilised by the formation, on the one hand, of a stilbenequinone, and on the other hand to a diphenylethane as shown in the following diagram. Obviously, the stilbenequinone may then undergo still more reactions resulting in more complex substances.



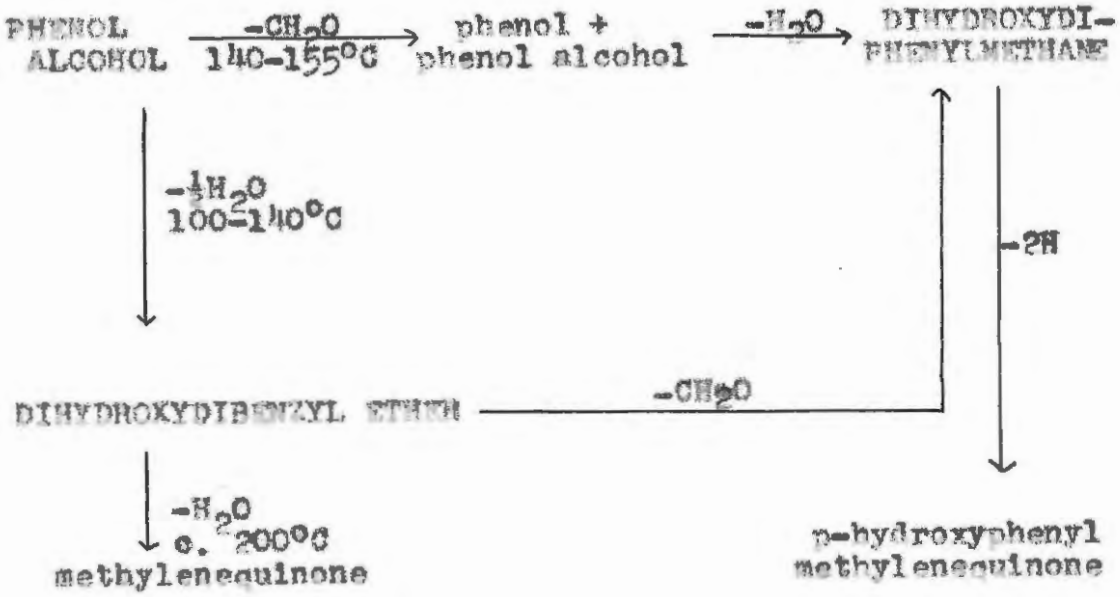
Substituted Stilbenequinone.

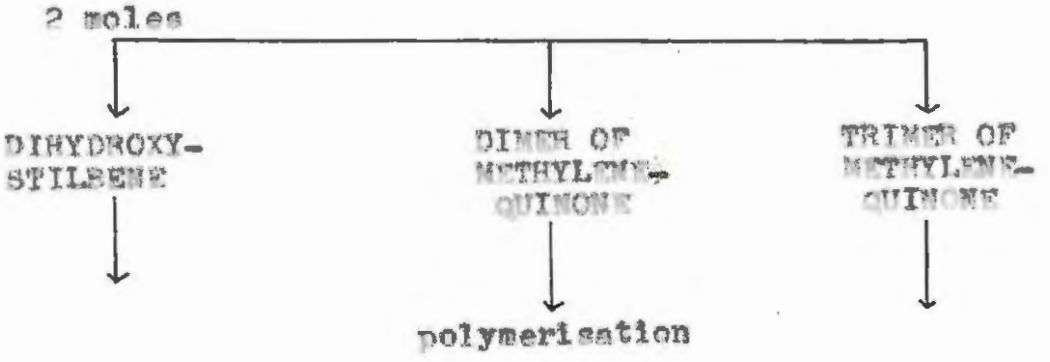
Substituted dihydroxy diphenyl ethane.

Both von Euler (31) and Hultzsch (32) claim that the formation of methylenequinone plays an important part in the hardening process through the reaction of phenol alcohols or their ethers with methylenequinone.



Zincke, Hultzsch and von Euler (33-35) have studied many reactions of the above nature. The results of their work may be tabulated as follows:





Many of the above reactions may take place only to a very limited extent in the case of phenols with three reactive positions. The formation of methylene

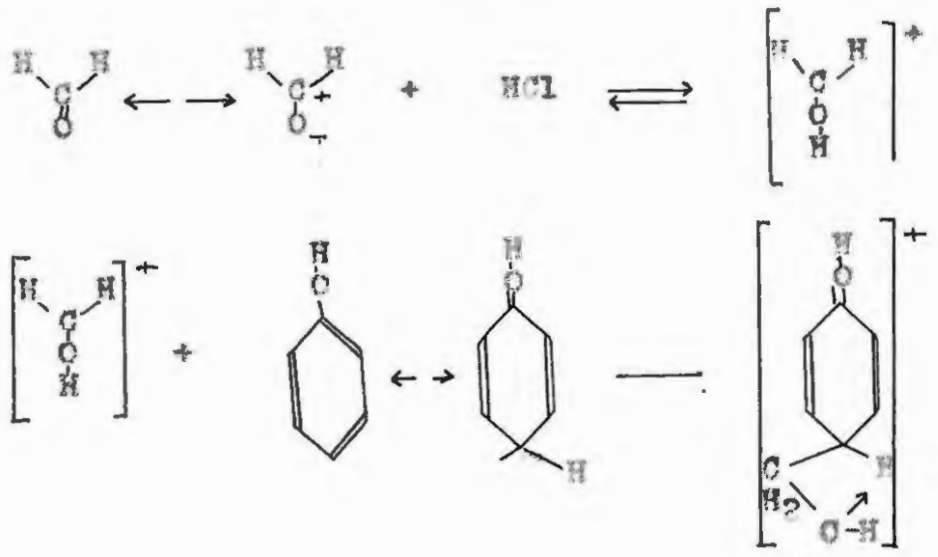
/linkages...

linkages appears to take place almost instantly from the dibenzyl ether linkages and so the cured resin has principally methylene bridges. To a certain extent it may contain some ethylene and stilbene linkages resulting from the reaction with methylenequinone bodies. The latter may also form large molecular aggregates by polymerisation. The resulting cured resin is cross-linked in the three dimensions and has a high molecular weight.

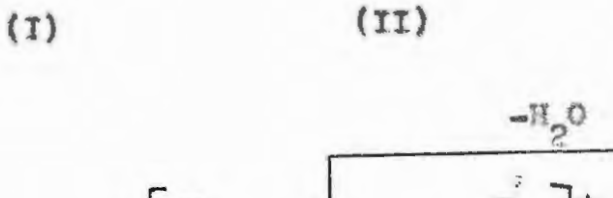
CONDENSATION IN ACID SOLUTION

From the work of Baekeland (37) and Ziegler (37) it seems probable that in acid solution the phenol alcohol forms but it condenses instantly under the influence of acid catalyst to give a diphenylmethane derivative.

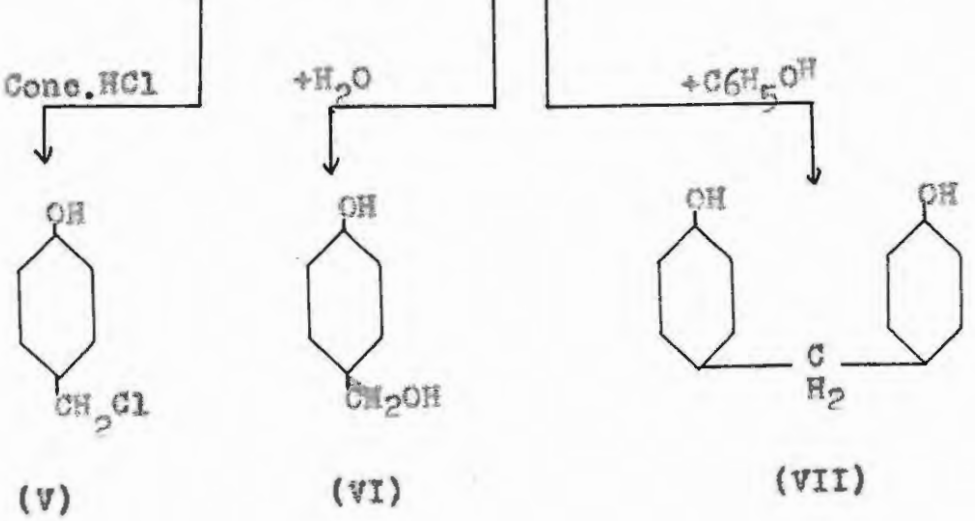
Hultzsch (27) suggested that the addition of formaldehyde to phenol takes place as follows:



(I) (II) (III)



(IV)

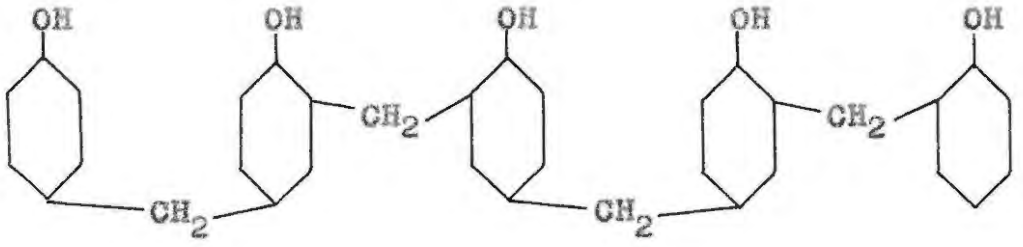


(V) (VI) (VII)

The formaldehyde molecule reacts with a hydrogen ion to form cation I which according to Eistert (38), joins with phenol II to form an intermediate compound III. Water splits off and highly reactive methylenequinone, derivatives IV form, which react with concentrated hydrochloric acid to give the chloromethyl derivative V, small quantities of the alcohol VI and, in the presence of phenol, the diphenylmethane derivative VII.

Although a phenol alcohol is probably formed when the phenol-formaldehyde reaction is either acid or alkali catalysed, the products which are obtained in the two reactions are entirely different.

When less than 0.86 moles of formaldehyde per mole of phenol is reacted in acid solution, the primary alcohols instantly condense to give a series of diphenylmethane chains, having from two to nine phenolic nuclei. These condensed products are called novolacs, and do not undergo further curing reaction unless more methylol groups are supplied. If excess formaldehyde is added insoluble macromolecules are formed, whose original linear molecular structure obviously changes to a three dimensional one. The structure for the novolac is:



The novolacs are permanently fusible and soluble but they can be further reacted (1) by condensation with formaldehyde in alkaline solution, when a resole is formed which then goes through the curing reactions previously described, (2) the novolac may be intimately mixed with hexamethylene tetramine, which on heating becomes a source of methylol groups.

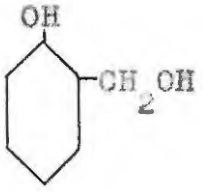
The fundamental difference between novolac and resole is the latter has one or more methylol groups in its structure

III. OUTLINE OF THE PRESENT WORK

OUTLINE OF PRESENT RESEARCH

INTRODUCTION

In the elucidation of the phenol-formaldehyde condensation, the starting point has invariably been the preparation of the methylol derivative of the phenol of the type.



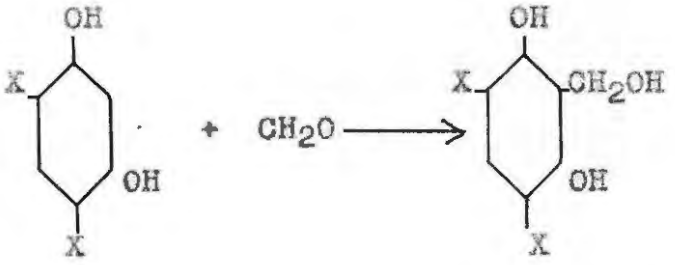
or identifiable compounds were extracted from the complex condensate. The former preliminary was adopted as a consequence of Baekeland's theory, that an alcohol is an intermediate in the formation of a phenol-formaldehyde resin. On the basis of that theory it was believed that, similarly, in the formation of resorcinol-formaldehyde resin, a resorcinyl alcohol, would be formed as a short-lived intermediate.

In the reaction of phenol and formaldehyde, condensation took place in the ortho and para positions, so it was accordingly assumed that condensation would be the same in the case of resorcinol.

On these two assumptions, it seemed possible that a resorcinyl alcohol might be produced by blocking two

/of.....

of the three reactive positions in the resorcinol molecule followed by reaction with formaldehyde

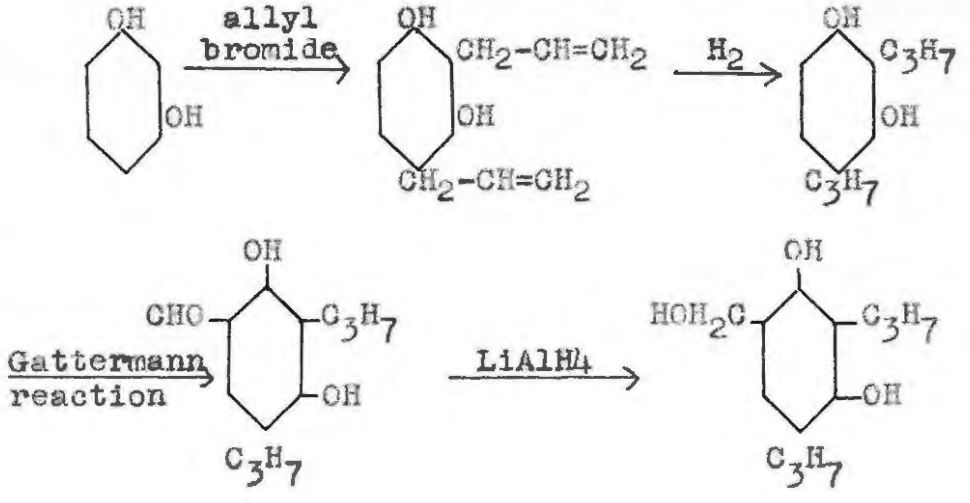
e.g. 

or by the introduction of the alcohol group in some other way.

To accomplish this, two methods were adopted, namely:

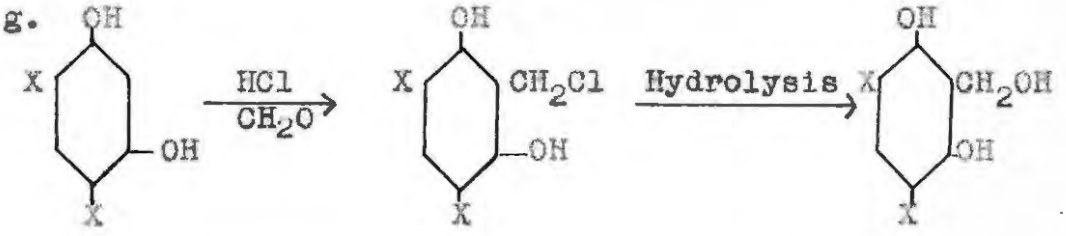
(1) Applying the mild reducing agent, lithium aluminium hydride on substances like 3,5-dibromo-β-resorcylaldehyde and 3,5-dibromo-β-resorcylic acid.

(2) Preparing a disubstituted resorcinol the substituent groups of which would not deactivate the phenyl nucleus nor cause steric hindrance, thereby interfering with the reaction that was being investigated. Ryding suggested the following preparation:



The resorcinyl alcohol might be prepared from the dialkyl resorcinol either by forming the aldehyde via the Gattermann reaction, or by chloromethylation followed by hydrolysis of the chloromethyl group to that of the alcohol

e.g.

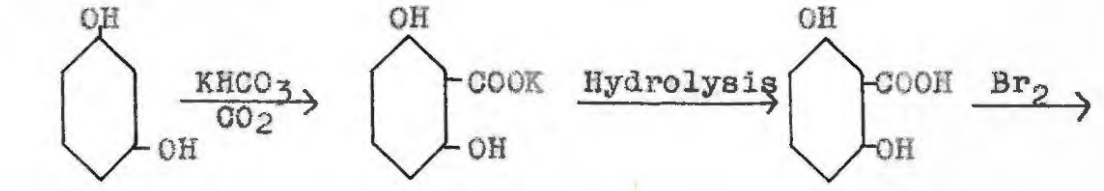


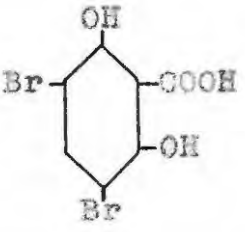
At the outset of this work it must be stressed that the understanding of the chemical structure of phenoplasts has been a difficult process because these plastics could not be examined by the usual analytical methods because of their susceptibility to being hardened by heating or by numerous chemical agents. Once hardened they become insoluble and infusible. It was only in the roundabout manner of studying model reactions that the chemistry of the phenoplasts formation could be investigated. A similar approach is, therefore, necessary in the case of the resorcinol-formaldehyde condensation.

A. ATTEMPTED REDUCTION OF SUBSTITUTED RESORCINOLS USING LITHIUM ALUMINIUM HYDRIDE

I. 3,5-DIBROMO-β-RESORCYLIC ACID

(1) Preparation





β-Resorcylic acid was prepared by the action of potassium bicarbonate and carbon dioxide on resorcinol. The resulting potassium salt was hydrolysed with concentrated hydrochloric acid to give β-resorcylic acid (39,40). The bromination was carried out by dissolving the acid in glacial acetic acid and adding bromine in the same solvent (41,42,43,44).

Ryding (26) condensed 3,5-dibromo-β-resorcylic acid with 40% formalin under alkaline conditions. A brown sludge was obtained. It was clearly shown from tests that the bromine groups had been removed and he suspected

/the.....

the formation of 2,3,4,5-tetrahydroxy benzoic acid. On chloromethylation of the acid Ryding suspected the formation of 4,4'-6,6'-tetrabromo-3,3'-5,5'-tetrahydroxy -2,2'-dicarboxyl diphenylmethane.

It was accordingly decided to attempt the reduction of the acid with lithium aluminium hydride.

(2) Reduction with lithium aluminium hydride

Lithium aluminium hydride has only recently become available as a mild reducing agent, though Nylstrom and Brown (45) indicated its importance in organic syntheses in 1947. Finn and Musty (46) successfully reduced a phenolic aldehyde to a phenolic alcohol with lithium aluminium hydride. Organic compounds containing halides have been reduced without affecting substituent halogen groups (47,48,49).

Judging from the experiments described in the above references, it seemed possible that 3,6-dibromo-β -resorcylic acid might be reduced to the dibromo resorcyl-aldehyde according to the equation.

$$2RCOOH + LiAlH_4 \longrightarrow LiAlO(OCH_2R)_2 + H_2O$$

$$\downarrow \text{hydrolysis.}$$

$$RCH_2OH$$

An ether solution of 3,5-dibromo-β-resorcylic acid was added slowly to lithium aluminium hydride dissolved in ether. A preliminary reaction took place resulting

/in.....

in the formation of a curdy white precipitate, and after the final addition, the solution separated into two layers - one creamy and the other ethereal.

Water was added to decompose the excess lithium aluminium hydride followed by the addition of dilute sulphuric acid to hydrolyse the metal alcoholate that might have formed. The curdy white precipitate disappeared. The ether layer was separated off and the aqueous layer extracted with ether. On evaporation of the ether, a precipitate remained. This was recrystallised from water. By means of a mixed melt it was proved that the substance was the original acid. The experiment also produced a brown material insoluble in water but the amount was so small that analysis was impossible.

The experiment was repeated using an increased amount of lithium aluminium hydride. The result was the same as before. This proved that lithium aluminium hydride does not reduce the acid group to the alcohol group on 3,5-dibromo-β-resorcylic acid.

II. 3,5-DIBROMO-β-RESORCYLALDEHYDE

(1) Preparation of β-resorcylaldehyde

β-Resorcylaldehyde was prepared by means of the Gattermann reaction by the method of Vogel (50). Resorcinol in ether was reacted with zinc cyanide and hydrogen chloride. The resulting aldimine hydrochloride

/was.....

was hydrolysed with boiling water to give the required aldehyde.

(2) Bromination of β-resorcylaldehyde.

The bromination was performed by the method of Ryding (26). To a solution of β-resorcylaldehyde in glacial acetic acid was added bromine in the same solvent. On stirring vigorously, a thick precipitate of 3,5-di-bromo-β-resorcylaldehyde was obtained.

(3) Reduction with lithium aluminium hydride

On using the recommended amount of lithium aluminium hydride (45), the original aldehyde was recovered. The experiment was repeated using an increased amount of lithium aluminium hydride.

It was necessary to incorporate a Soxhlet extractor as the aldehyde was only slightly soluble in ether. When all the aldehyde had been reacted with lithium aluminium hydride, excess lithium aluminium hydride was eliminated by addition of water, and the intermediate was hydrolysed by the addition of dilute sulphuric acid. On evaporation of the combined ether layer and ether extracts, a reddish brown substance, which had a non crystalline resinous appearance, resulted.

The product was found to be insoluble in water or chloroform but soluble in a number of organic solvents.

/The.....

The compound was repeatedly dissolved in a solvent or mixed solvents in an attempt to form a crystalline compound but only transparent amber-coloured flakes of irregular form appeared. Acetylation or benzoylation failed to produce derivatives.

Ryding (26) attempted to reduce 3,5-dibromo-β-resorcylaldehyde using a number of different reducing agents. He found that the catalytic hydrogenation using platinum oxide as catalyst yielded a red gum. It was analysed but no positive structure could be ascribed to it. He came to the conclusion that the red gum was a resin.

Carothers (51) reduced β-resorcylaldehyde to obtain a gum.

In the reduction of 3,5-dibromo-β-resorcylaldehyde with lithium aluminium hydride, it was noticed during the course of one run a white precipitate was formed after hydrolysis by the addition of dilute sulphuric acid. Unfortunately the precipitate only lasted for a short period and then changed to a red gum. Possibly the bromine groups were removed during the course of the reaction, and, subsequently, by the action of the sulphuric acid, the alcohol condensed to form a resin.

It was thereupon decided to prepare di-alkyl resorcinols and produce the requisite resorcinyl alcohol therefrom.

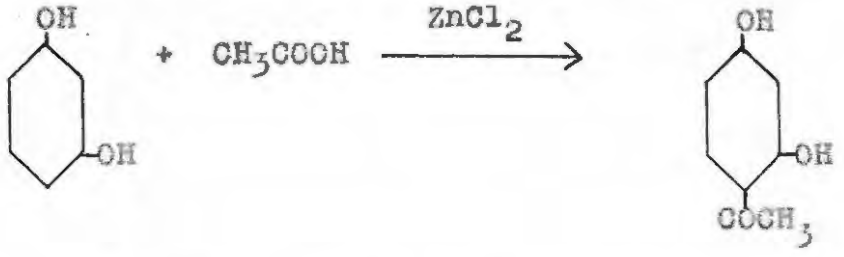
B. ATTEMPTED PREPARATION OF A DI-ALKYL RESORCINOL ALCOHOL

I. 2-METHYL-4-ETHYL RESORCINOL

(1) Preparation

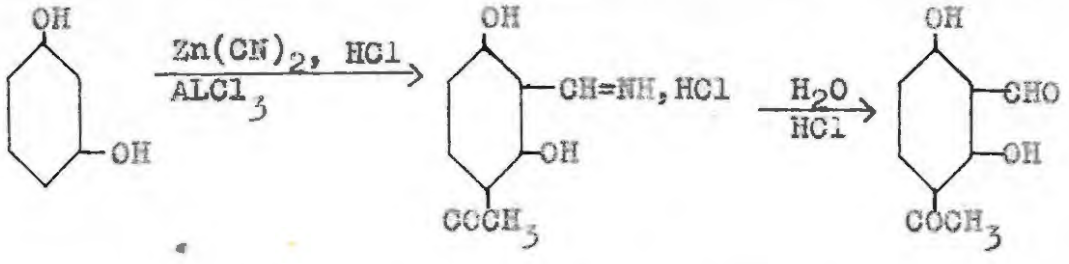
The preparation of this compound was accomplished in a three stage synthesis.

(a) Preparation of resacetophenone (52,53).



To zinc chloride dissolved in glacial acetic acid, resorcinol was added slowly whilst stirring and heating. On diluting with hydrochloric acid and cooling in ice, orange-yellow crystals of resacetophenone crystallised out.

(b) Preparation of 2,4-dihydroxy-3-formyl acetophenone (54)

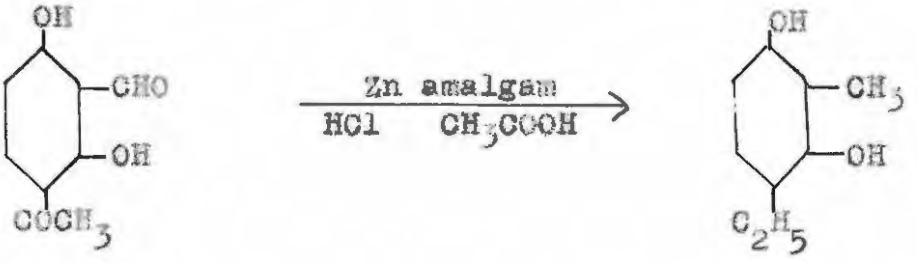


To a solution of resacetophenone in dry ether was added zinc cyanide and potassium chloride followed by

/aluminium.....

aluminium chloride dissolved in dry ether. The aldimine hydrochloride was formed by passing dry hydrogen chloride through the mixture. After 20 hours in the ice-chest, the yellow pasty aldimine hydrochloride was washed with ether after which water was added. The aldimine hydrochloride was hydrolysed to the aldehyde which separated out in the form of orange crystals.

(c) Preparation of 2-methyl-4-ethyl resorcinol (54)



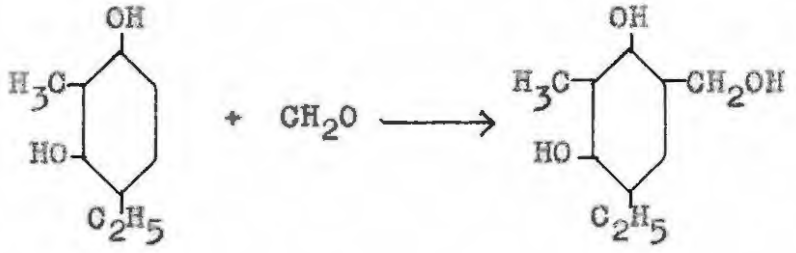
2,4-Dihydroxy-3-formyl acetophenone was reduced by Clemmensen's reduction. It was added to zinc amalgam, dilute hydrochloric acid and acetic acid. The mixture was heated and stirred. The product was extracted with ether and purified by vacuum distillation and recrystallisation from high boiling point petrol ether.

(2) CONDENSATION OF 2-METHYL-3-ETHYL RESORCINOL WITH FORMALDEHYDE

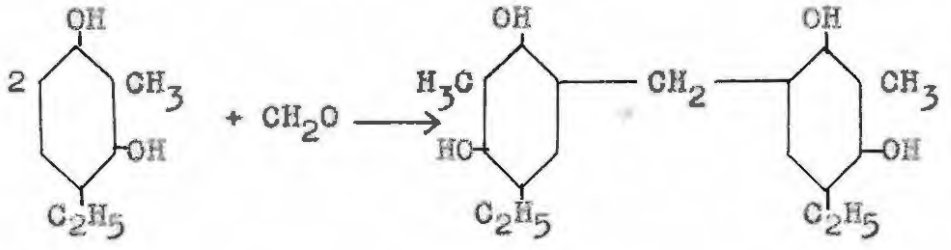
2-Methyl-4-ethyl resorcinol has two of the three ortho-para positions blocked leaving one ortho-para position

/and...

and one meta position unsubstituted. It was expected that on reaction with formaldehyde an alcohol group would be substituted in the remaining ortho-para position as follows:



or alternatively that the diphenylmethane derivative would form thus:



2-Methyl-4-ethylresorcinol was reacted with formaldehyde according to the Manasse reaction (55). The dialkyl resorcinol was dissolved in dilute sodium hydroxide and formaldehyde added. On standing for three days the solution turned deep red and was neutralised with dilute acetic acid. A yellowish gelatinous precipitate formed. Examination under the microscope proved the precipitate to be non-crystalline. On filtration a yellowish clay-like substance was obtained which dissolved in ethanol. On evaporation this solution yielded a

/clear.....

clear reddish compound, amorphous and without melting point. Instead, it charred and ignited at a high temperature.

The clay-like substance hardened either on drying at room temperature or when heated. This hardened substance was insoluble in concentrated hydrochloric acid and only slightly soluble in ethyl alcohol.

According to Granger (56), this formation of a gelatinous precipitate (which, on filtration and drying out, hardens to a dark brittle substance, decreasing in volume is practically insoluble in concentrated sodium hydroxide)is a very strong indication of resin formation.

The condensation was also carried out in an acid medium. The dialkyl resorcinol was added to dilute hydrochloric acid, heated and formaldehyde added. A red oil resulted which hardened on cooling. Again the product was only slightly soluble in ethanol and sodium hydroxide and had no melting point. Resin formation was assumed to have taken place.

(2) CHLOROMETHYLATION.

A new approach for preparing the alcohol of 2-methyl-4-ethylresorcinol was then adopted. An attempt was made to prepare the chloromethyl derivative which could subsequently be hydrolysed to the alcohol.

A solution of formalin and concentrated hydrochloric

/acid.....

acid was saturated with hydrogen chloride gas and the dialkyl resorcinol added. Reaction took place yielding a black resinous mass. The black substance dissolved in alcohol which, on evaporation yielded an amorphous resin.

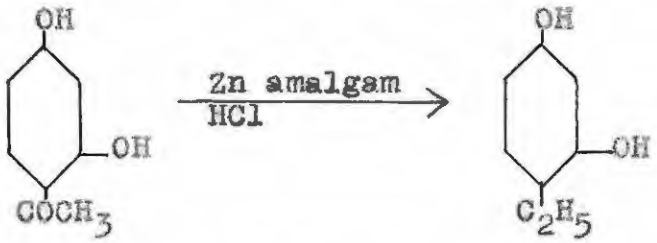
II. 4,6-DI-ETHYLRESORCINOL

The preparation of di-ethylresorcinol was carried out simultaneously with that of 2-methyl-4-ethylresorcinol as the latter was found to be a very prolonged synthesis. It is interesting to compare the result of the reaction between di-ethylresorcinol and formalin with that of 2-methyl-4-ethylresorcinol and formalin.

Preparation of di-ethylresorcinol

This substance was prepared in a 4-stage synthesis.

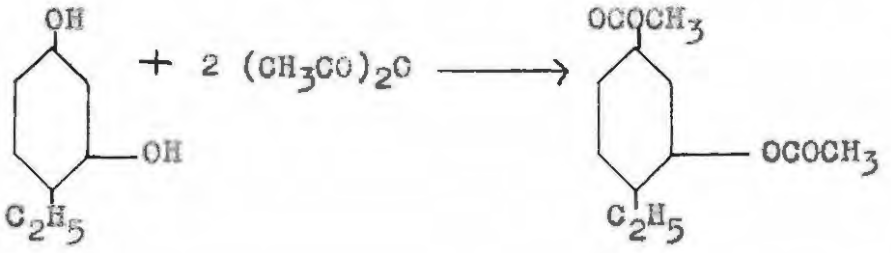
(a) Preparation of 4-ethylresorcinol.



The synthesis of resacetophenone has already been described. When this substance is refluxed with dilute hydrochloric acid and zinc amalgam, it is reduced to 4-ethylresorcinol.

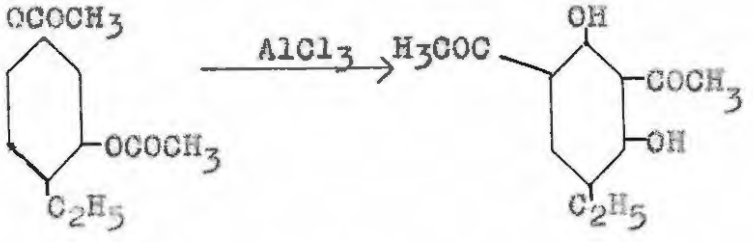
/(b).....

(b) Preparation of 4-ethylresorcinoldiacetate (57)



4-ethylresorcinol was boiled with excess acetic anhydride. The resulting mixture was shaken with water extracted with ether which, on evaporation, yielded a liquid, which was dried and vacuum distilled. A colourless liquid, 4-ethylresorcinoldiacetate, resulted.

(c) Preparation of 4-ethyl-2,6-diacetateresorcinol (58)



Ethylresorcinoldiacetate was dissolved in nitrobenzene, cooled in ice and aluminium chloride added. It was heated and dilute hydrochloric acid added. The nitrobenzene was removed by steam distillation and the product extracted with ether and purified by vacuum distillation.

(d) Preparation of 4,6-di-ethylresorcinol (58)

This substance was prepared by reducing 4-ethyl-2,6-deacetylresorcinol, using the Clemmensen reduction. The acetyl group in the 2-position split off, and the acetyl group in the 4-position was reduced to the ethyl group.

(2) CONDENSATION OF 4,6-DI-ETHYLRESORCINOL WITH FORMALDEHYDE

According to the Manasse (55) reaction 4,6-diethyl-resorcinol was dissolved in dilute sodium hydroxide, formaldehyde added and the solution allowed to stand. On neutralisation with acetic acid, a gelatinous precipitate formed which dissolved in alcohol and resulted in a brittle red, amophous substance on evaporation of the alcohol. It had no melting point but charred on heating.

The result was the same as in the reaction between 2-methyl-4-ethylresorcinol and formaldehyde.

Di-ethylresorcinol was treated with formalin using hydrochloric acid as catalyst. A red oil resulted which,

/on....

on keeping, transformed into a hard insoluble resin.

Chloromethylation was performed in the same manner as in the case of the last dialkylresorcinol. The result was the same and a similar resin was formed.

C. REACTION OF FORMALDEHYDE WITH DI-ISOHEXYLRESORCINOL

The arrival of this red viscous oil, obtained through Poly Resin Ltd., from the U.S.A., prompted further research using di-alkylresorcinol before tri-alkyl resorcinol was investigated.

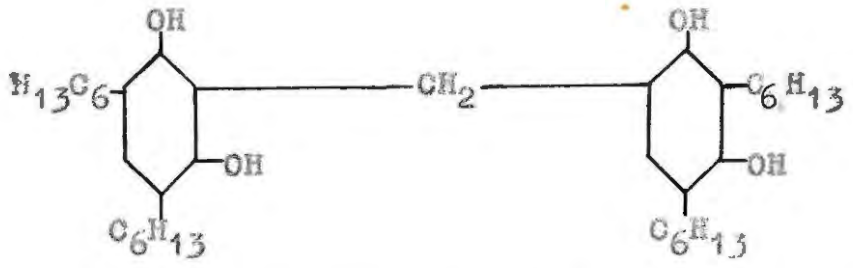
(a) Manasse reaction

It was necessary to use a solution of sodium hydroxide stronger than the usual 1% to dissolve the compound. Even then solution did not take place completely. Formalin was added and the solution left for a few days. The undissolved oil gradually turned dark red in colour and the solution reddish white, indicating the presence of a precipitate. At the end of the stated period, there remained a brown precipitate, a certain amount of red oil and a red supernatant liquid. On neutralisation with dilute hydrochloric acid, the liquid lost its red colour.

The precipitate was non-crystalline and had a melting point of 165-175°C. The molecular weight was determined by the elevation of the boiling point of ethyl alcohol and found to be 517. The calculated molecular

/weight.....

weight of the diphenylmethane derivative of isohexyl-resorcinol



was 568. Considering that the method used for determining the molecular weight was not very accurate, when high molecular weights were determined, the result was an indication that the suggested compound had formed. That a resin was not formed in the case of this dialkyl-resorcinol could be ascribed to the fact that the alkyl groups are extremely large and thus steric hindrance could prevent condensation at the meta position.

(b) CHLOROMETHYLATION

1. The method of chloromethylation used by Finn and Musty (59) was adopted.

Di-isohexylresorcinol was dissolved in ethyl acetate, formaldehyde added and hydrogen chloride passed through the solution. The substance formed was a brownish green jelly, which dried out to a hard black resinous compound. The substance was insoluble in organic solvent and sodium hydroxide. It did not melt but charred at 400°C. An alternative method of chloromethylation was tried.

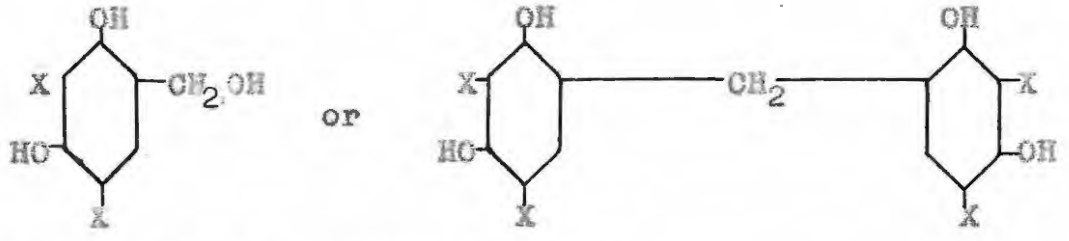
/2. .....

2. This was a new technique in chloromethylation which proved very successful in later experiments.

The di-isohexylresorcinol was dissolved in ethyl acetate and added to a solution of concentrated hydrochloric acid, concentrated sulphuric acid and formaldehyde. A brown solid formed. It was soluble in ethyl alcohol from which it reprecipitated on the addition of water. It softened at 180°C but the molecular weight proved to be close on 5,000 indicating that resin formation had taken place.

CONCLUSION

When blocking resorcinol in two of the three ortho and para positions, it was expected that, in the reaction with formaldehyde, either of the following compounds would be formed:



where X is the substituent group.

Using four different di-substituted resorcinols viz. 3,5-dibromo-β-resorcylic acid, 3,5-dibromo-β-resorcylaldehyde, 2-methyl-4-ethylresorcinol and 4,6-diethylresorcinol attempts were made to produce either

/the.....

the resorcinyl alcohol or the diphenylmethane compound. Ryding (26) made several similar attempts to prepare a resorcinyl alcohol from di-substituted resorcinol. In every case, either no reaction occurred, or resin formation took place.

When dichloro resorcinols were used, it would be understandable for the resin formation to result, because of the splitting off of the chlorine groups, but the breaking away of alkyl groups would be less likely. In the two cases where alkyl groups were used to block two of the three ortho and para positions, resin could only form if condensation were taking place either through the hydroxyl groups or at the meta position. The former is unlikely - the latter quite possible. In the investigations carried out on the phenol-formaldehyde condensation, reaction through the hydroxyl group was never found to take place. Although it was suspected that condensation could result in the meta positions of phenol to some small degree, resin formation did not take place when 2 of the 3 ortho and para positions were blocked. Apparently in the case of resorcinol, the meta position is more reactive, as condensation definitely takes place there. This may account for the fact that resorcinol condenses with formaldehyde under less drastic conditions of temperature and catalyst than in the case of phenol.

/The.....

The next stage in this investigation was an attempt to prepare the resorcinyl alcohol of 2,4,6-trimethyl-resorcinol (mesorcinol) using formalin. In other words an attempt was made to prove that formaldehyde does condense in the meta position of resorcinol.

TRIMETHYL RESORCINOL

When any two positions, including the meta position, are unsubstituted in the benzene ring of resorcinol, it reacts with formaldehyde under acid or alkaline conditions to form a resin, when the substituted groups are either ethyl or methyl. This has been established by experiments already described.

To prove that formaldehyde condenses with resorcinol in the meta position, it was necessary to prepare 2,4,6-trimethylresorcinol.

2,4,6-trimethylresorcinol, or mesorcinol, had been prepared by Cornforth and Robinson (60). Their method was to heat a solution of resorcinol in sodium methoxide at 220°C for ten hours in an autoclave. They acidified the resulting solution and after steam distillation, reduced the volume under vacuum. Light yellow crystals of mesorcinol deposited.

As no autoclave was available, an hydrogenator was substituted. This latter apparatus, however, was extremely cumbersome and took 6 hours to heat to the required temperature of 220°C. The full reaction took some 16 hours to complete. The first two runs yielded a red tar. A glass container was made to fit the hydrogenator so as to prevent the solution coming into contact with the copper lining of the hydrogenator. The

/resulting....

resulting solution was acidified with dilute hydrochloric acid, steam distilled to remove methanol and unreacted resorcinol and clarified with animal charcoal. On reducing the volume under vacuum, a solid precipitated. This was purified by sublimation and produced flat pointed needles with a melting point of 150°C, and it reduced silver nitrate. These properties were the same as found by Knecht (61) and later by Cornforth and Robinson (60), in their experiments with mesorcinol.

The combustion results and the molecular weight determination performed on the product obtained indicated that the compound was mesorcinol.

The above method of preparation was unsatisfactory as it took too long and the yield was very small.

A bomb was made out of mild steel to withstand a pressure greater than 850 lbs per square inch - the pressure developed during the reaction.

The reaction solution was poured into a large glass test tube which was placed in the bomb. The bomb was heated in an oven which maintained a constant temperature. Under the correct conditions the yield of mesorcinol was found to be 31%.

On recrystallising the crude mesorcinol from benzene, a substance was found to be present which was insoluble

/in.....

in benzene. This was probably the resorcylic acid which Cornforth and Robinson suspected was formed (60). A certain amount of red tar was usually present after the reaction. This could have resulted from condensation of resorcinol and formaldehyde formed from methanol during the course of the reaction. The formation of a certain amount of formaldehyde was suspected since on occasions, when the bomb leaked, its presence could be detected by smell.

The crude mesorcinol was also purified by sublimation but a considerable loss of compound was incurred in the operation.

II. THE REACTION OF MESORCINOL WITH FORMALDEHYDE

(a) The following experiment yielded the first positive result in the investigation of the resorcinol-formaldehyde reaction. A new compound was formed which was not a resin.

Mesorcinol was dissolved in dilute sodium hydroxide solution, a small quantity of formalin added and the solution left to stand for ten days. It was then acidified. No precipitate formed immediately, so it was left for a further two days. The result was a slight precipitate of tiny spheres composed of needles converging to the centre. The substance had a melting

/point.....

point which varied from 160-180°C. The mixed melt with mesorcinol gave a depression of melting point, indicating that a new substance had formed. This product was soluble in most organic solvents. Whereas it was insoluble in cold water, it dissolved in boiling water, but took a few days to crystallise from the cooled water, and much was lost. These difficulties were increased by the fact that, at this stage, the yield of mesorcinol was very low.

The combustion results for the crude compound were not conclusive. Under these conditions of poor yield, lengthy preparation, and purification difficulties, it was essential to find a more satisfactory method of preparing the resorcinyl alcohol.

In 1950 Finn and Musty (59) found that the alcohol 5-hydroxymethyl-2,4,6-trimethylphenol, could not be prepared by direct combination of mesitol and formaldehyde in alkaline solution or in alcoholic sodium ethoxide solution; in each case mesitol was recovered quantitatively unchanged. In the case of mesorcinol, however, a new but impure compound was formed when either method was used.

(b) Chloromethylation

An attempt was made to prepare the resorcylic alcohol via the chloromethyl derivative by the hydrolysis

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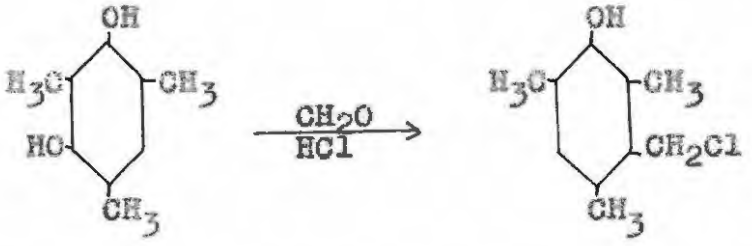
of the latter.

The chloromethyl derivative of 2,4,6-trimethylphenol had been prepared by Finn and Musty (59). Their method of preparation was thereupon adopted using mesorcinol.

(1)



Mesorcinol was dissolved in ethyl acetate, and, after the addition of formalin, hydrogen chloride was passed through the solution. On evaporation of the ethyl acetate a brownish solid was obtained. On purification a white solid was extracted. The melting point was 196°C. The presence of chlorine was established and then determined quantitatively (62). The percentage of carbon was established by combustion and the molecular weight determined by the elevation of boiling point of benzene. This analytical data indicated that the compound was 5-chloromethyl-2,4,6-trimethylresorcinol. This was a new compound as it was not described in the literature.

/ (2).....

(2) A NEW TECHNIQUE OF CHLOROMETHYLATION OF PHENOLIC COMPOUNDS.

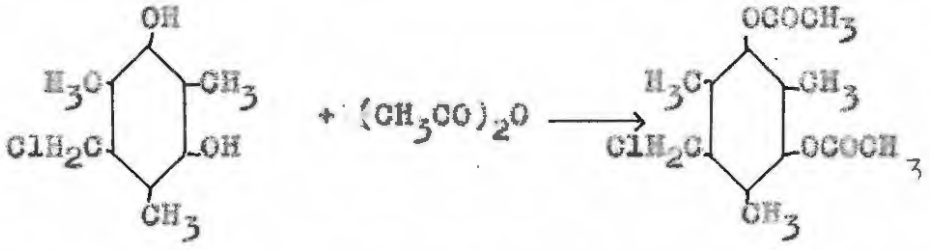
The problem of poor yield of 5-chloromethyl-2,4,6-trimethylresorcinol was overcome by performing the reaction between mesorcinol, formaldehyde and hydrochloric acid under conditions as anhydrous as possible.

Concentrated hydrochloric acid was added very carefully to concentrated sulphuric acid until HCl gas just ceased to be generated. Formalin was added, followed by a saturated solution of mesorcinol in either ethyl acetate or ethyl alcohol. On stirring, a precipitate of fine needles formed almost immediately. The substance was filtered and washed with water. When pure mesorcinol was used, a pure product was obtained.

The melting point was 197-8°C., the mixed melt with chloromethylmesorcinol gave no depression. From the analytical results there was no doubt that this substance was 5-chloromethyl-2,4,6-trimethylresorcinol.

The striking point about this preparation was that the yield was 95%.

III. PREPARATION OF 1,3-ACETOXY-5-CHLOROMETHYL-2,4,6-TRIMETHYLRESORCINOL.



The method of acetylation used by Finn and Musty (59) was adopted. The chloromethyl derivative was suspended in acetic anhydride and solution took place on the addition of a few drops concentrated sulphuric acid. After standing overnight water was added when an oil formed which crystallised on standing.

From microcombustion, chlorine determination and molecular weight data, it was established that the acetate of the chloromethyl derivative had been prepared.

The yield was 60% and the melting point 135-7°C. The crystals obtained from one preparation were colourless, elongated, prismatic, hexagonal, uni-axial positive and the refractive index was greater than 1.

IV. PREPARATION OF 2,4,5,6-TETRAMETHYLRESORCINOL

The object of preparing tetramethylresorcinol from the chloromethyl derivative was to substantiate the structure of the latter.

(a) Attempted preparation

Finn and Musty (59) prepared tetramethylphenol in a certain way, so it was considered that tetramethyl resorcinol might be prepared in a similar way.

1,3-acetoxy-5-chloromethyl-2,4,6-trimethylresorcinol was dissolved in acetone and refluxed with zinc and concentrated hydrochloric acid. The ether extract was refluxed with alcoholic sodium hydroxide, and the resulting solution was acidified and steam distilled. The product which precipitated neither possessed the properties of tetramethylresorcinol described by Bauer-Benedkt (63), nor did the combustion results indicate that the product was tetramethylresorcinol. Accordingly a more direct method of preparation was attempted.

(b) Preparation.

5-Chloromethyl-2,4,6-trimethylresorcinol was dissolved in ethanol and added to freshly prepared zinc amalgam. Hydrochloric acid was added and the solution refluxed on a water-bath. On cooling or reducing the volume, thick irregular colourless needles formed. The compound could be purified by vacuum sublimation or recrystallisation. Its properties agreed accurately with those described for tetramethylresorcinol by Bauer-Benedikt and Punzengruber (63) and the microcombustion and molecular weight results confirmed the structure of this compound.

The above method of preparation of tetramethylresorcinol is simpler and the yield better than that described by Bauer-Benedikt and Punzengruber, as will be seen from the following tables:

/THEIR.....

THEIR PROCEDURE		PRESENT PROCEDURE	
Compound	Yield	Compound	Yield
Orcin	-	Resorcinol	-
Orcylaldehyde	40%	Mesorcinol	31%
4,5-Dimethyl resorcinol	54%	5-Chloromethyl resorcinol	95%
2,3-Dimethyl-4,6-dioxy benzaldehyde	85%	Tetramethyl resorcinol	85%
4,5,6-Trimethyl resorcinol	80%		
3,4,5-Trimethyl-2,6-dioxy benzaldehyde	80%		
Tetramethyl resorcinol	66%		

(c) Another preparation of tetramethylresorcinol

Tetramethylresorcinol was also prepared from 5-hydroxymethyl-2,4,6-trimethylresorcinol (a new compound to be described later).

The method of preparation was the same as that described above in section (b) except that 5-hydroxymethylmesorcinol was used instead of 5-chloromethylmesorcinol.

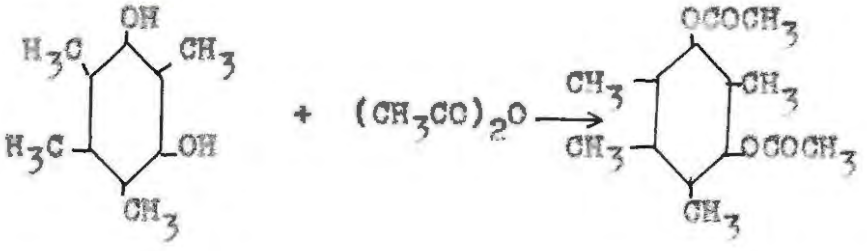
/Again.....

Again the importance of this reaction lay in the fact that it confirmed the structure of the starting material.

B. DERIVATIVES OF TETRAMETHYLRESORCINOL

Bauer-Benedikt and Punzengruber (59) first prepared tetramethylresorcinol, but in their paper they do not describe any derivatives, so two derivatives have been prepared.

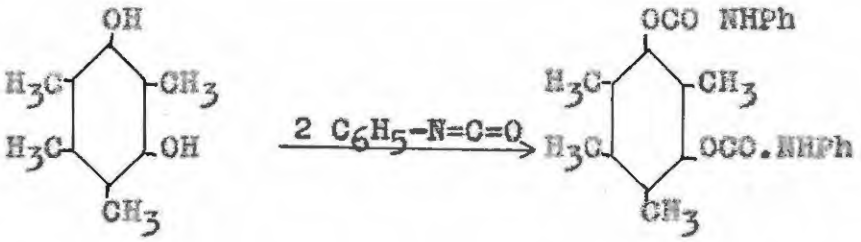
(a) Preparation of 1,3-acetoxy-2,4,5,6-tetramethyl resorcinol



Tetramethylresorcinol was acetylated by dissolving it in acetic anhydride, adding a few drops of concentrated sulphuric acid and allowing to stand overnight. On adding this solution to excess water an oil formed which crystallised on standing. The product was recrystallised from acetone-water solution and colourless needles of melting point 98.5 - 99.5°C. were obtained. A microcombustion substantiated the structure of the compound.

/(b)....

(b) Preparation of the phenylurethane of tetramethylresorcinol



A mixture of tetramethylresorcinol and phenylisocyanate was heated on a water bath. After solution had taken place the heating was continued when reaction took place and the mixture set to a solid mass. After purification the melting point was found to be 235-7°C. and microcombustion and nitrogen estimation data established the structure of the compound.

V. 5-HYDROXYMETHYL-2,4,6-TRIMETHYLRESORCINOL

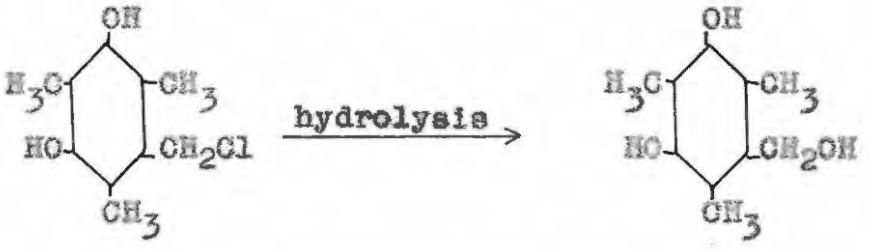
It was thus established that 5-chloromethyl-2,4,6-trimethylresorcinol had been prepared. From this compound it was hoped to prepare 5-hydroxymethyl-2,4,6-trimethylresorcinol. With this alcohol it would be possible to investigate the condensation reaction between resorcinol and formaldehyde since according to theory when unsubstituted resorcinol condenses with formaldehyde it combines with the latter to form a short-lived intermediate, a resorcinyl alcohol which immediately condenses to form macromolecules - the resorcinol-formaldehyde condensate.

(a) Attempted preparation

The chloromethyl derivative was shaken with freshly prepared silver oxide in ethyl alcohol. It was expected that the required alcohol and silver chloride would form. After filtering only a small amount of brown gum was obtained on evaporating the ethyl alcohol. This method of preparation was abandoned.

/(b).....

(b) Preparation



Finn and Musty (59) prepared a phenol alcohol by hydrolysis of the chloromethyl derivative of a substituted phenol. Their method was adopted.

The chloromethylresorcinol was dissolved in water-dioxan mixture and a few marble chips were added and the solution refluxed on a water bath. Some difficulty was experienced in the precipitation of the alcohol derivative and attempts to recrystallise the compound failed. It was, however, possible to prepare a pure product which did not require recrystallisation.

The combustion results were not entirely satisfactory but a molecular weight determination indicated that the compound was 5-hydroxymethyl-2,4,6-trimethylresorcinol. This was confirmed by the preparation and analysis of derivatives.

From a mixed melt with the compound described in section II (a), it was established that they were

/the.....

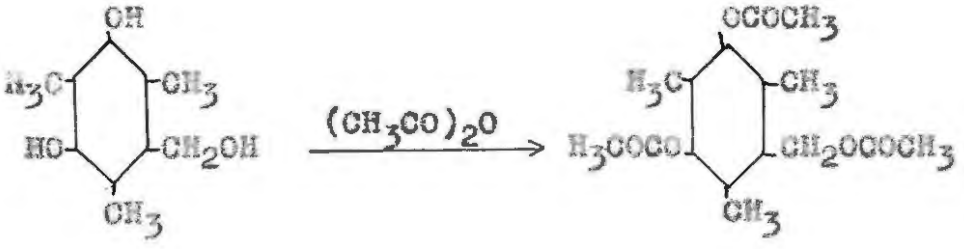
the same substance. In other words when resorcinol and formaldehyde react in alkaline medium a resorcinyl alcohol is formed. This result was predicted by the phenol-formaldehyde theory.

(c) Reconversion to chloromethyl derivative

The resorcinyl alcohol was dissolved in ethyl acetate then added to a mixture of concentrated hydrochloric and sulphuric acids. Immediately fine needles of 5-chloromethylmesorcinol formed. This was established by means of a mixed melt with the authentic substance.

PREPARATION OF DERIVATIVES OF 5-HYDROXYMETHYL-2,4,6-TRIMETHYLRESORCINOL

(d) (i) Preparation of the acetate



The resorcinyl alcohol was reacted with acetic anhydride. Anhydrous potassium carbonate was added to absorb any water that was present. When reaction was complete, water was added dissolving all but the required acetate. After recrystallisation colourless needles, with melting point 118-119°C, were formed.

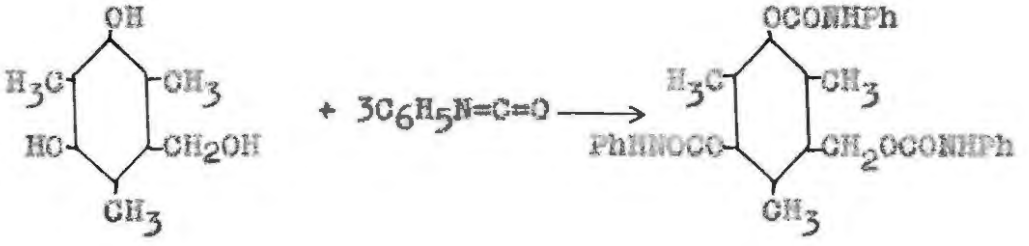
/Microcombustion.....

Microcombustion and molecular weight determinations established the structure of the acetate and, therefore, of the resorcinyl alcohol.

(d) (ii) Attempted preparation of the acetate

An attempt was made to prepare the acetate by the reaction of 5-chloromethyl-2,4,6-trimethylresorcinol with silver acetate in water and acetic acid. The two mixtures were shaken together. The excess silver was eliminated by the addition of hydrochloric acid. After filtering and vacuum distilling the filtrate, a brown gum was obtained and recrystallised from water-acetone solution to give a very small quantity of colourless needles with a melting point of 106° - 108°C. This preparation was, however, abandoned since the reaction required the extravagant use of silver acetate and it took too much time.

(e) Preparation of the triphenylurethane derivative



The resorcinyl alcohol and the phenyl-iso-cyanate

/were.....

were heated on a flame until reaction took place by the solidification of the liquid. The mixture was left overnight then purified. The white compound had a melting point of 224-5°C. The microcombustion and nitrogen estimation results confirmed the structure of the compound.

VI. 1,1'-3,3'-TETRAHYDROXY-2,2'-4,4'-6,6'-HEXAMETHYL-DIPHENYLMETHANE

It is a well known fact that when phenol condenses with formaldehyde in acid medium the diphenylmethane derivative forms in preference to the phenyl alcohol. Accordingly an attempt was made to show that resorcinol condensed with formaldehyde in an acid medium to form the diphenylmethane compound.

(a) Preparation

Difficulty was experienced in the preparation of the diphenylmethane compound since invariably a brown oil was obtained which would not crystallise. It was eventually found that the amount of acid present had to be carefully controlled and the amount of water present limited.

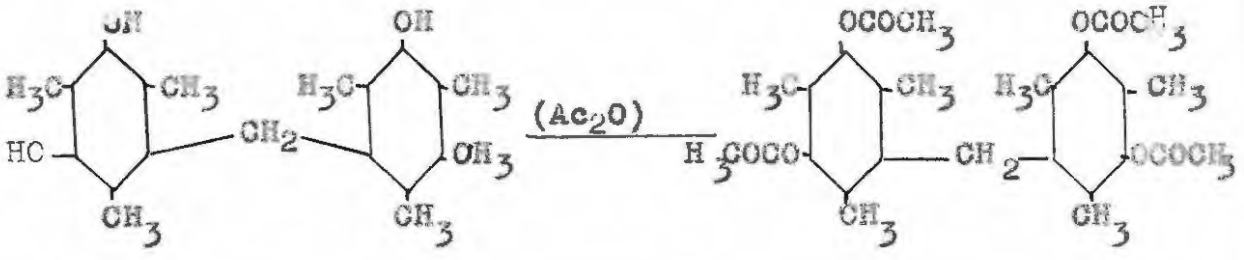
Resorcinol was dissolved in ethyl alcohol and formaldehyde added and the solution heated. Concentrated hydrochloric acid was added drop by drop until

/an.....

an oil formed. On cooling a brown precipitate was obtained. Even then the compound had to be recrystallised several times before a sharply melting compound was obtained. The melting point was 229-231°C. The percentage carbon obtained by microcombustion did not coincide with the calculated percentage carbon for the diphenylmethane compound but the molecular weight determination and the preparation of the acetate derivative established the formula of this compound.

DERIVATIVES OF THE DIPHENYLMETHANE COMPOUND

(a) Preparation of the acetate



The diphenylmethane was dissolved in acetic anhydride and anhydrous potassium carbonate added to produce the anhydrous condition necessary for completion of the reaction. On addition of water everything dissolved except the acetate. This derivative was recrystallised from dilute ethyl alcohol and had a melting point of 185-187°C. The microcombustion proved compound to be 1,1'-3,3'-tetramethoxy-2,2'-4,4'-6,6'-hexamethyldiphenylmethane.

/ (c).....

Preparation of the tetraphenyl urethane derivative

The diphenylmethane compound was reacted with phenyl-iso-cyanate by heating. The resulting solid dissolved in dioxan. It was intended to reprecipitate the derivative by addition of water, but when this was done an oil resulted which would not crystallise. This was thought to be due to the impure diphenylmethane compound used. Shortage of time and material did not permit complete investigation.

VII. REACTIONS OF 5-HYDROXYMETHYL-2,4,6-TRIMETHYL-RESORCINOL

This next stage in the investigation of the resorcinol formaldehyde condensation was important but time did not allow for thorough experimentation. The resorcinyl alcohol had been prepared and since it was thought that the resorcinyl alcohol is an intermediate in the resorcinol formaldehyde condensation, the next logical step was to attempt to condense the alcohol with resorcinol or substituted resorcinols. This condensation, according to Little and Pepper (23) who suggested that the resorcinol formaldehyde condensation might be catalysed by either hydrogen or hydroxyl ions, should take place in either an acid or alkaline medium.

/ (1).....

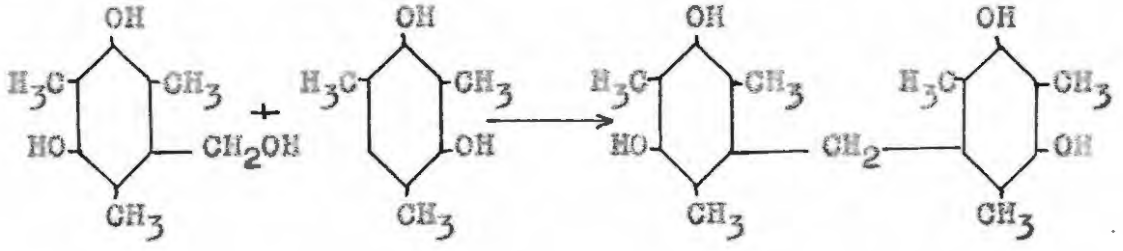
(1) Condensation with 2,4,6-trimethylresorcinol

(a) Under alkaline conditions.

The alcohol and excess mesorcinol were dissolved in dilute sodium hydroxide and heated. On neutralisation a gum was formed. This was dissolved in ethyl alcohol and water was added. A brown precipitate settled out on standing. It had a melting point of 130°C.

Unfortunately only small quantities of reactants were in hand so only a small amount of the product could be made which was insufficient for purification and analysis.

(b) Under acidic conditions.



The alcohol and excess mesorcinol were dissolved in ethyl alcohol and dilute hydrochloric acid added. After heating for two hours on a water bath a precipitate of brown needles formed. It had a melting point of 227-229°C. A mixed melt with the genuine 1,1'-3,3'-tetrahydroxy-2,2'-4,4'-6,6'-hexamethyldiphenylmethane

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gave a melting point of 226-228°C. This result proved that the resorcinyl alcohol had condensed with mesorcinol to form the diphenylmethane compound.

(2) Condensation with resorcinol

(a) Under alkaline conditions

Equal weights of the resorcinyl alcohol and resorcinol were dissolved in sodium hydroxide and left to stand. On acidifying no precipitate formed, so the solution was ether extracted. This yielded a red oil which took three days to start crystallising.

(b) Under acid conditions

The two reactants were dissolved in ethanol, acid was added. The solution was extracted with ether and a red oil was obtained which also started to crystallise on standing.

These red oils were not subjected to investigation. It was, however, suspected that condensation had taken place between resorcinol and the resorcinyl alcohol to produce a red oil. Since resorcinol has 4 positions on the benzene ring at which condensation could take place, the red oil would be a mixture of a number of condensation products.

IV CONCLUSIONS

The experiments by Ryding (26) and those carried out in the present work, with the intention of forming a β - or γ -resorcinyl alcohol from a disubstituted resorcinol, resulted in resin formation. A number of both 2:4- and 2:6-disubstituted resorcinols were reacted with formaldehyde. There are two possible explanations for the unexpected resin formation:
(1) Reaction took place at the 5- (or meta) position.
(2) There was interaction between resorcinyl molecule, through their substituents.

By the study of the reactions of 2:4:6-trimethylresorcinol, it became obvious that the first explanation, at least, was true. 2:4:6-trimethylresorcinol, with one free position on the benzene ring, reacted with resorcinol to form the diphenylmethane derivative, whilst under alkaline conditions, there was no positive evidence of reaction. It was, therefore, apparent that, in this case, the alkyl groups did not enter into the condensation.

5-hydroxymethyl-2:4:6-trimethylresorcinol reacted with resorcinol under both acid and alkaline conditions.

From these results, it was possible to envisage resin formation, in the reaction of a 4:6-dialkylresorcinol and formaldehyde, as taking place in the

/following.....

following manner:

(a) Under acid conditions

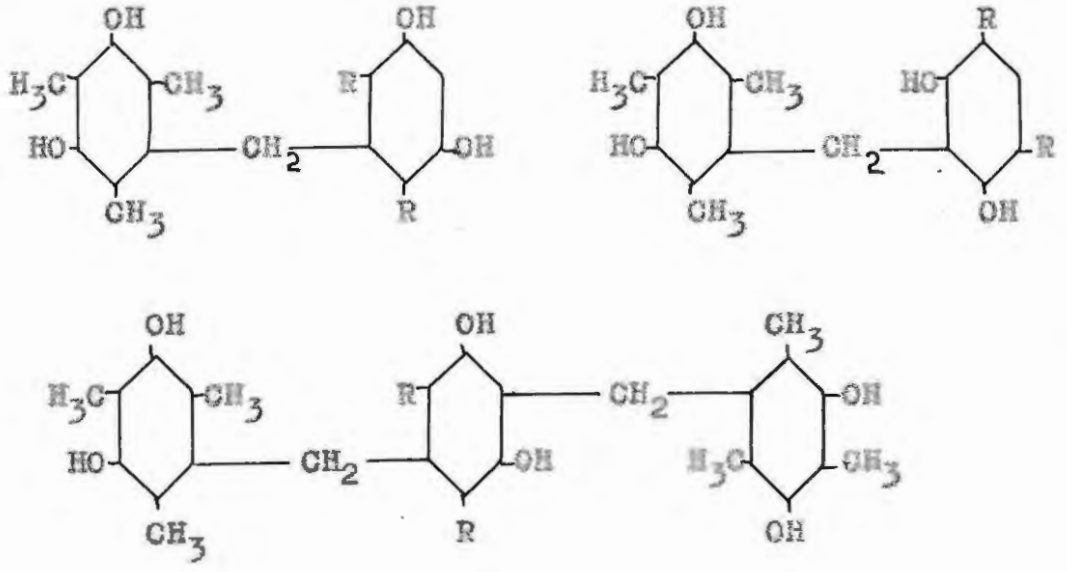
Diphenylmethane formation can take place at both the 2- and 5-positions. 4:6-dialkylresorcinol, therefore, is bifunctional and a novolac-type resin can result.

(b) Under alkaline conditions

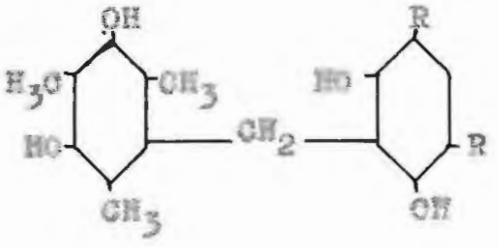
Methylol formation can occur at the 2- and 5-positions. The methylol group will presumably form preferentially at the 2-position since it is ortho to the hydroxy groups. Condensation can then take place involving the 5- and 2-positions. The methylol groups which form at the 5-position can condense at the 2-position only, but in any case the phenol is effectively bifunctional and resin formation will occur.

A similar argument holds in the case of a 2:4 dialkylresorcinol.

These hypotheses could be tested in the following manner. In the first place 5-hydroxymethyl-2:4:6-trimethyl-resorcinol could be reacted with dialkyl-resorcinol. Under acid conditions, three compounds could form



whereas under alkaline conditions, only one could form, since the 5-hydroxymethylol group in the 5-position would only react with the free ortho position of the disubstituted resorcinol:



The thorough study of the reaction between 5-hydroxymethyl-2:4:6-trimethylresorcinol and resorcinol. with four free positions on the phenyl nucleus, would be more complicated, since there are a great number of combinations that could result.

/The.....

The next step would be to form 4:5:6- or 2:5:6-trisubstituted resorcinol, and to prepare the respective β- or γ- hydroxymethyl derivatives and to study the reactivity of these alcohols.

From these trisubstituted resorcinols, a series of new compounds could be formed in exactly the same way as was done for mesorcinol.

The resorcinyl alcohol was prepared by reaction of mesorcinol with formaldehyde under alkaline conditions. It is interesting to note that Finn and Musty (59) were unable to prepare the phenyl alcohol from 2:4:6-trimethylphenol in this way i.e. under alkaline conditions. This indicates that resorcinol is more reactive than phenol when condensed with formaldehyde under alkaline conditions. The greater reactivity of resorcinol in this condensation is further supported by the fact that dialkylresorcinol reacts with formaldehyde to form a resin whereas disubstituted phenols have been reacted with formaldehyde to form phenyl alcohols and no resin formation took place.

VI. EXPERIMENTAL.

A. ATTEMPTED REDUCTION OF SUBSTITUTED RESORCINOLS USING LITHIUM ALUMINIUM HYDRIDE

I. 3-5 DIBROMO-β-RESORCYLIC ACID

(1) Preparation (page 25)

By the action of potassium bicarbonate and carbon dioxide on resorcinol in aqueous solution, a potassium salt was produced. This salt when hydrolysed with concentrated hydrochloric acid yielded β-resorcylic acid (39, 40).

The bromination of β-resorcylic acid was carried out by dissolving the acid in glacial acetic acid, and to the solution was added three moles bromine dissolved in the same solvent (41, 42, 43, 44).

(2) REDUCTION WITH LITHIUM ALUMINIUM HYDRIDE. (page 26)

Apparatus

The method was a modification of that used by Nylstrom and Brown (45). A clean dry 100 ml. round bottom double necked flask was fitted with a dropping funnel and a reflux condenser. Calcium chloride tubes were attached to exclude moisture.

Method

To 0.1 gm. lithium aluminium hydride in the flask were added 2 ml. dry ether via the dropping funnel. A solution of 1.3 gms. 3-5 dibromo-β-resorcylic acid in

/10 ml. .....

10 ml. ether was added slowly whilst shaking. A curdy white precipitate formed immediately, accompanied by vigorous evolution of gas. By the time the final addition was made, a certain quantity of brownish substance had formed.

A small amount of water was added to decompose excess lithium aluminium hydride, followed by 15 ml. 10% sulphuric acid to hydrolyse the metal alcoholate (45). The precipitate dissolved in the solution and the ether was separated from the aqueous layer, which was extracted twice with ether. The ether was dried, filtered and evaporated. There remained brownish crystals which were recrystallised from water. The melting point of the purified product and its mixed melt with the original acid proved that it was 3-5 dibromo-β-resorcylic acid.

A very small amount of brown material was separated from the product during recrystallisation. This could have been the desired alcohol, so the experiment was repeated using 1 gm. instead of 0.01 gm. lithium aluminium hydride. The result was the same as in the previous experiment.

/ II. .....

II. 3-5 DIBROMO-β-RESORCYLALDEHYDE. (page 27)

The Gattermann reaction was employed for the preparation of the aldehyde according to the method of Vogel (50).

(2) BROMINATION OF β-RESORCYLALDEHYDE (page 28)

This preparation was carried out according to the method of Ryding (26).

To 1 mole of β-resorcylaldehyde in glacial acetic acid were added 3 moles of bromine, also in glacial acetic acid, and the solution was stirred vigorously. A thick precipitate was obtained and filtered off.

(3) REDUCTION OF 3-5 DIBROMO-β-RESORCYLALDEHYDE WITH LITHIUM ALUMINIUM HYDRIDE. (page 28)

Apparatus:

A triple-necked round bottom flask was fitted with a mercury sealed stirrer, a Soxhlet extractor and a dropping funnel.

Method:

4 gms. 3-5 dibromo-β-resorcylaldehyde were placed in the cup of a Soxhlet extractor. This was done because the aldehyde was found to be only partially soluble in ether. 3 gms. lithium aluminium hydride were placed in the flask. 15 ml. dry ether were

/added.....

added and the solution allowed to reflux on a water bath until the aldehyde dissolved.

With the first overflow of the aldehyde in ether, there was vigorous reaction accompanied by the formation of a creamy precipitate.

The unchanged lithium aluminium hydride was eliminated by the addition of a little water followed by 50 ml. 10% sulphuric acid in order to hydrolyse the metal alcoholate that might have formed. The precipitate which settled soon turned brown. Extraction with ether yielded a dark-red resinous substance which was soluble in methyl and ethyl alcohol, ethyl acetate and acetone and insoluble in water and chloroform.

The red solid would not recrystallise from any solvents or solvent mixtures that were tried. It could be reprecipitated from a solution by adding water and also by acidifying an alkaline solution of the substance with acetic acid. The substance appeared to be amorphous.

Attempts to benzoylate and acetylate the hydroxy groups of the substance failed.

B. ATTEMPTED PREPARATION OF A DI-ALKYL RESORCINOL ALCOHOL

I. 2-METHYL-4-ETHYL RESORCINOL

The preparation of this compound was accomplished

/in.....

in a three stage synthesis.

(1) (a) PREPARATION OF RESACETOPHENONE. (page 30)

10 gms. of powdered zinc chloride were dissolved in 110 gms. glacial acetic acid by heating (52). The solution was placed on a sandbath and the temperature regulated to 142°C., when 75 gms. resorcinol were added. The temperature was increased to 152°C. (boiling point). Heating was thereupon discontinued and the solution left on the sandbath for 20 minutes.

The reaction mixture was diluted with 330 ml. (1:1) hydrochloric acid and cooled to 5°C., when orange-yellow crystals of resacetophenone formed. The yield was 70 gms. and melting point 142°C.

The reacetophenone was purified by vacuum distillation at 180/10 mm. or by recrystallisation from 900 ml. (1:1) hydrochloric acid.

(b) PREPARATION OF 2-4 DIHYDROXY-3-FORMYLACETOPHENONE (page 30)

Apparatus

The apparatus suggested by Vogel (50) was used for the generation of dry HCl gas. A 1000 ml. round bottom flask with a large neck was used for the reaction. The flask was fitted with an inlet tube having a lipped end to prevent clogging and a

/mercury.....

mercury sealed stirrer. An outlet tube was attached to a funnel inverted into an alkaline solution to absorb HCN gas evolved during the reaction.

Method:

The method devised by Shah and Shah (54) was adopted. 30 gms. resacetophenone were dissolved in 500 ml. sodium dried ether and the solution cooled in a freezing mixture. To this was added 46 gms. zinc cyanide, prepared according to the method of Vogel (50). 50 gms. dry potassium chloride were added to increase the yield of the final product from ether. 50 gms. aluminium chloride were dissolved carefully in 200 ml. dry ether and added to the solution. Dry HCl gas was passed through the stirred solution for 7 hours.

After 24 hours in the refrigerator, the ether was decanted and the orange-yellow paste, namely the aldimine hydrochloride, was washed well with ether. 200 ml. water were added and the solution heated on a water bath for 30 minutes. This brought about the hydrolysis of the aldimine hydrochloride to the required aldehyde. A yield of 20 gms. was obtained and the product was recrystallised from water-alcohol solution.

/ (c).....

(c) PREPARATION OF 2-METHYL-4-ETHYLRESORCINOL (page 31)

The method of Shah and Shah (54) was followed. Zinc amalgam was prepared by adding 5 gms. mercury chloride and dilute hydrochloric acid to 30 gms. zinc dust. After thorough washing with distilled water, 50 ml. (1:1) hydrochloric acid and 10 ml. glacial acetic acid were added and the solution heated on a water bath.

5 gms. 2,4-dihydroxy-3-formylacetophenone were dissolved in alcohol and introduced slowly. Every hour an extra 3 ml. hydrochloric acid were added. The solution was left to reflux until the ethereal extract of a sample of the liquid produced no coloration with alcoholic ferric chloride. This occupied 7 hours.

The hot solution was filtered, cooled and extracted with ether. On evaporation of the ether, a brownish oil remained. The oil was then vacuum distilled and a clear oily liquid, which slowly crystallised to a pearly lustrous solid, resulted. It was recrystallised from high boiling point petrol ether and had a melting point of 86°C.

/ (2) .....

(2) CONDENSATION OF 2-METHYL-4-ETHYLRESORCINOL WITH FORMALDEHYDE. (page 31)

(a) Alkaline condensation:

The Manasse reaction was employed.

1 gm. of 2-methyl-4-ethylresorcinol was dissolved in 100 ml. 1% sodium hydroxide and an excess (6 ml.) of formalin added. The solution was left to stand for three days. On neutralisation with dilute acetic acid, a gelatinous precipitate formed. On filtering, a clay-like amorphous substance was obtained which hardened and reduced in volume on drying. This substance frothed up and charred on heating to a high temperature. It was partially soluble in organic solvents and sodium hydroxide.

When the experiment was repeated, using only 1 ml. formaldehyde, the result was the same.

(b) Acid condensation

1 gm. of the dialkylresorcinol was added to 50 ml. dilute hydrochloric acid and heated. On the addition of 1 gm. formalin, a red oil resulted, which hardened on cooling. The product was a hard red substance with no definite melting point, amorphous and only partially soluble in organic solvents and sodium hydroxide.

/ (3) .....

(3) Chloromethylation

30 ml. concentrated hydrochloric acid and 1 ml. formalin were saturated with dry HCl gas, prepared according to the method of Vogel (50). 1 gm. of the dialkylresorcinol was added and immediately there resulted a dark, hard, brittle and granular mass. It was insoluble in solvents and sodium hydroxide, and so was taken to be a resin.

II. 4,6-DIETHYLRESORCINOL (page 34)

The various stages in the preparation of this compound were as follows:

Stage (a) The preparation of resacetophenone

The preparation of resacetophenone has already been described on page 71.

Stage (b) The preparation of 4-ethylresorcinol

10 gms. resacetophenone were dissolved in 50 ml. dilute hydrochloric acid and 5 gms. zinc amalgam (prepared by treating zinc dust with mercuric chloride and dilute hydrochloric acid) added. The solution was refluxed for about 4 hours, cooled, filtered and extracted with ether. The refluxing time was established in accordance with the method of Fieser and Adams (66) namely that a colour test was performed.

/A.....

A few drops of alcoholic ferric chloride were added to the ether extract of a sample of the solution. The completion of the reduction was established when this colour test was no longer green but yellow.

The ether extract of the solution was dried over sodium bicarbonate. The crude 4-ethylresorcinol was purified by vacuum distillation at 180/12 mm.

It was re-established (as other investigators had found) that 4-ethylresorcinol had no definite melting point.

Stage (c) The preparation of 4-ethylresorcinol diacetate

The method of Lothian and Baker (57) was followed.

4-Ethylresorcinol was boiled with an excess of acetic anhydride for 2 hours. The mixture was shaken with water and extracted with ether. The extracts were then shaken with aqueous sodium sulphate. On vacuum distillation of the oil obtained on the evaporation of the ether, 4-ethylresorcinol diacetate distilled over at 162°C/4 mm. as a colourless liquid.

Stage (d) Preparation of 4-ethyl-2,6-diacetylresorcinol

The method of Rosenmund, Buchwald and Deligianus (58) was followed.

10 gms. 4-ethylresorcinol diacetate were dissolved in 25 ml. notrobenzene. The solution was cooled in ice before adding 2.1 moles aluminium chloride. It

/was.....

was then heated for 3-4 hours to 60 - 70°C. Crushed ice and dilute hydrochloric acid were added carefully to eliminate the unchanged aluminium chloride, and the solution was steam distilled to remove the nitrobenzene. The ether extract was filtered, dried and evaporated. The product was purified by vacuum distillation. Bright yellow crystals of 4-ethyl-2,6-diacetylresorcinol with a melting point of 74°C. resulted.

Stage (e) Preparation of 4,6-diethylresorcinol

The Clemmensen reduction was employed. 5 gms. 4-ethyl-2,6-diacetylresorcinol were dissolved in 20 ml. dilute hydrochloric acid and 15 gms. zinc amalgam (prepared according to the method described in stage (b)) added. The solution was refluxed for 5 hours and was then filtered and extracted with ether. After evaporation of the ether, the product was purified by vacuum distillation at 150°C/10 mm. 4,6-diethylresorcinol was obtained.

(2) CONDENSATION OF 4,6-DIETHYLRESORCINOL WITH FORMALDEHYDE (page 36)

The condensation of diethylresorcinol with formaldehyde was carried out in precisely the same way as in the case of 2-methyl-4-ethylresorcinol (see section B I (2) and (3) of the Experimental) namely under

/alkaline.....

alkaline conditions and acidic conditions, and chloromethylation was attempted.

Each of the three experiments resulted in the production of a resin.

The resins produced from the dialkylresorcinols had the following properties. They were only slightly soluble in organic solvents. In ethanol a red solution was obtained but portions of the resin remained undissolved. A molecular weight determination by the elevation of the boiling point of ethanol (65) failed, since, even with a large excess of ethanol, some solvent remained undissolved and the elevation produced was negligible. The resin did, however, dissolve in phenol after prolonged boiling. A molecular weight determination was thereupon attempted using phenol as the solvent. The necessity for boiling the phenol, rendered accurate results impossible, since it was essential, in an experiment of this nature, to keep the solution out of contact with the air. The results were so divergent that no positive conclusions could be drawn.

The resins were found to amorphous and did not melt but charred on heating to about 400°C.

/C. .....

C. REACTION OF FORMALDEHYDE WITH DI-ISOHEXYLRESORCINOL

(page 37)

(a) Alkaline condensation

½ gm. of the red viscous oil, di-isohexylresorcinol was shaken with 20 ml. sodium hydroxide. Only a portion of the oil went into solution. 1 ml. formalin was added and the solution was left to stand for three days.

The undissolved oil turned dark red and the solution showed signs of precipitation.

The solution was thereupon neutralised with dilute hydrochloric acid and the precipitate filtered off. Re-precipitation was performed several times by adding water to a solution of the compound in ethyl alcohol. It was a reddish-brown non-crystalline compound. The melting point was 165 - 175°C.

Molecular weight.

The molecular weight of the product was determined cryoscopically using the Menzies-Wright apparatus. The method of Rae and Reilly (65) was used with the following modifications:

Instead of determining the elevation produced by dissolving weighed pellets of the substance in a weighed amount of the solvent, an undetermined amount of solvent was used and a comparison was made of the

/elevations.....

elevations produced by adding to it weighed pellets of benzil and the above product alternately. Since the molecular weight of benzil is accurately known, the molecular weight of the unknown substance was calculated by simple proportion, assuming there was no interaction between the two solutes. The actual elevations of temperature recorded on the differential thermometer were read by means of a sliding microscope.

Ethyl alcohol was used as solvent and to check the accuracy of the method, the molecular weight of benzil was determined.

Results:	Benzil	Benzil	New Compound
Weight of substance	0.1210 gm.	0.1399 g.	0.1072 gm.
Elevation in boiling point	0.480	0.562	0.175
Molecular weight found	-	207.4	516.6

Benzil has a molecular weight of 210 so that the method gave a good indication of the true molecular weight. The diphenylmethane derivative of di-isohexyl resorcinol, $C_{37}H_{60}O_4$, has a theoretical molecular weight of 568, so that it appears that this compound might have formed.

/ (b) .....

(b) Chloromethylation

The method of chloromethylation used by Finn and Musty (67) was adopted. 5 gms. di-isohexylresorcinol were dissolved in 40 ml. ethyl acetate and 3 ml. formalin were added and HCl gas passed through the solution for 2 hours. The container was corked and the solution allowed to stand overnight.

The product was a brownish green jelly and was washed several times by decantation first with boiling water and then with boiling petrol ether. On drying the purified product in air there remained lumps of black substance which were insoluble in solvents and sodium hydroxide, were amorphous and charred at a temperature of 400°C. An alternative technique of chloromethylation was attempted.

2. 2 gms. di-isohexylresorcinol were dissolved in 10 ml. ethylacetate and this solution added to a mixture of 20 ml. concentrated sulphuric acid, 10 ml. concentrated hydrochloric acid and 3 ml. formalin. A brown solid formed almost immediately. The acid solution was diluted with water and the precipitate filtered off. The precipitate was partly soluble in ethyl alcohol. This alcoholic solution was filtered and water added to the filtrate. A fine reddish-brown precipitate formed which softened at 180°C.

/MOLECULAR.....

MOLECULAR WEIGHT

The molecular weight was determined as described in section C (a).

	Benzil	Benzil	New Compound
Weight of substance	0.1515gm.	0.1532gm.	0.1003gm.
Elevation in boiling point	0.623	0.638	0.020
Molecular weight found	-	207.5	4,383

This high molecular weight indicated that a resin had formed.

D. I. PREPARATION OF 2,4,6-TRIMETHYLRESORCINOL

(a) Using an hydrogenator

The method was based upon that of Cornforth and Robinson (60), but in the absence of an autoclave, an hydrogenator with the hydrogen inlet closed, was adopted.

12 gms. pure sodium metal were reacted under reflux, with 150 ml. methanol, the reaction flask being cooled with water. 10 gms. resorcinol were dissolved in the sodium methoxide solution and this solution was poured into a glass cylinder which was placed in the hydrogenator. The temperature was raised to 220°C. and maintained for 10 hours.

/The.....

The variations of temperature with pressure during the experiment were as follows:

HEATING TIME hours	TEMPERATURE ^{o}C	PRESSURE $lbs/in.^2$
1	163	240
2	177	280
3	191	380
4	200	470
5	214	600
6	218	650
9	219	790
$10\frac{1}{2}$	220	850

The pressure remained fairly constant at 850 lbs/ins^2 with the temperature at $220^{o}C$.

After allowing the hydrogenator to cool, the reaction solution was removed, neutralised with hydrochloric acid and steam distilled to remove unreacted methanol and resorcinol. A large amount of sticky reddish gum was formed. After purification of the solution with animal charcoal and reducing the volume of the solution by vacuum distillation, a very poor yield of mesorcinol was obtained.

The experiment was tried six times but an hydrogenator was found to be unsatisfactory.

/ (b).....

(b) Using a steel bomb

The pressure developed during the reaction was found to be 850 lbs/square inch, so a bomb, strong enough to withstand a greater pressure, was constructed. Its inner cavity 13×4 cms. was turned out of a cylinder of mild steel 17 cms. long and 8 cms. in diameter. The lid was fastened by means of 6 bolts and a copper washer interposed. It was found necessary to anneal the copper washer after each run.

The purification of the methanol by fractional distillation was essential, as any trace of water interfered with the preparation. The resorcinol was dried before use.

9 gms. sodium metal were reacted with 100 ml. methanol under reflux to give sodium methoxide. 8 gms resorcinol were added, the solution stirred and poured into a glass tube which fitted loosely in the bomb. The lid was bolted securely and every precaution taken to prevent leakage. The bomb was placed in an oven set at 218^{O}C and left for 8 hours. After removal, the apparatus was allowed to cool before opening. The resulting solution was washed out of the tube and the bomb, and neutralised with dilute hydrochloric acid.

Unless the foregoing procedure was carefully followed the yield of mesorcinol was negligible, if any

/at.....

at all.

The solution was steam distilled, clarified with charcoal and the volume reduced by boiling under vacuum. On cooling and standing mesorcinol crystallised out.

The best yield obtained was 40% but the successful preparations averaged only 30% yield.

The mesorcinol was purified by recrystallisation from benzene or water or by vacuum sublimation. On employing the latter method, flat pointed needles of whitish colour were obtained. The other two methods produced a fairly pure yellow product. The melting point was 151°C. The substance reduced silver nitrate.

COMBUSTION RESULTS

(1) 0.1219 gms. of compound gave 0.3045 gms. CO_2 and 0.0879 gms. H_2O

%C = 68.13%, %H = 8.01%

(2) 0.1004 gms. compound gave 0.2603 gms CO_2 and 0.0784 gms. H_2O

%C = 70.71%, %H = 8.67%

Mean %C = 69.43%, %H = 8.34%

For $C_9 H_{12}O_2$, %C = 71.0%, %H = 7.9%

/MOLECULAR.....

MOLECULAR WEIGHT

The molecular weight was found cryscopically by the depression of the freezing point of phenol according to the method of Finn (67).

Weight of phenol = 18.56 gms.
Weight of compound = 0.1506 gms
Depression in freezing point = 0.398°C
Molecular weight = 152.9

For mesorcinol, $C_9H_{12}O_2$, the molecular weight is 152.

II. REACTION OF MESORCINOL WITH FORMALDEHYDE. (page 42)

(a) Alkaline condensation

½ gm. mesorcinol purified by vacuum sublimation was dissolved in 50 ml. 1% sodium hydroxide and 1 gm. 40% formaldehyde added. The solution was left for 10 days, acidified and left for a further 2 days, during which a precipitate formed. After filtering the solution the precipitate was thoroughly washed with distilled water. The melting point of the compound was 180-181°C and the mixed melt with mesorcinol was 138 - 168°C, indicating the formation of a new compound.

A combustion was attempted but the substance did not burn easily.

/COMBUSTION.....

COMBUSTION RESULTS

0.0903 gms substance gave 0.2095 gms CO_2 and 0.0586 gms. H_2O .

%C = 63.27%, %H = 7.21%

For 5-hydroxymethyl-2,4,6-trimethylresorcinol, $C_{10}H_{14}O_2$,

%C = 65.9%, %H = 7.21%,

The yield of the product was very low — ½ gm. from 4 gms. mesorcinol. Attempts to recrystallise the substance failed. It was soluble in ethanol, methanol and acetone. It was insoluble in cold water but dissolved in boiling water, but did not recrystallise on cooling.

(b) CHLOROMETHYLATION (page 45)

(1) The method of chloromethylation used by Finn and Musty (59) to chloromethylate mesitol was applied.

One gm. mesorcinol was dissolved in 8 ml. ethyl acetate. To this was added 0.5 ml. 40% formaldehyde. HCl gas was passed through the solution for two hours after which the flask was corked and left overnight. A brown precipitate resulted which was purified by recrystallisation from petrol ether.

The product was an amorphous white substance and

/had.....

had a melting point of 190 - 200°C. It was recrystallised from ethyl acetate and then gave a melting point of 196°C.

The yield of the pure derivative was very low.

(2) The following is a new technique in chloromethylation which proved to be extremely simple and successful.

About 50 ml. concentrated sulphuric acid were placed in an 800 ml. beaker in a fume cupboard. Concentrated hydrochloric acid was added carefully until no further effervescence of HCl gas occurred. 4 ml. 40% formaldehyde were added, followed by a concentrated solution of 3 gms. mesorcinol in 5 ml. ethyl acetate. On stirring, the solution quickly became cloudy and fine needles formed. The solution was left to stand for five minutes, then 500 ml. water were added and the solution filtered and washed ten times with distilled water under vacuum.

It was found that if pure mesorcinol was used in the preparation and the product washed thoroughly, a pure derivative was obtained. The yield was 95% and the melting point 197 - 8°C. A mixed melt with the substance prepared by the above method gave no depression.

/PERCENTAGE.....

PERCENTAGE CHLORINE

0.2046 gms. substance gave 0.1411 gms. silver chloride.

%Cl = 17.06%

For 5-chloromethyl-2,4,6-trimethylresorcinol, $C_{10}H_{13}O_2Cl$,

%Cl = 17.70%

COMBUSTION RESULTS

0.1620 gms. substance gave 0.3620 gms. CO_2 and 0.0989 gms. H_2O .

%C = 60.94%, %H = 6.8%

For $C_{10}H_{13}O_2Cl$

%C = 60.0%, %H = 6.50%

MICROCOMBUSTION RESULT

The following result was obtained by Weiler and Strauss (64):

4.454 mg. substance gave 9.785 mg CO_2 and 2.500 mg H_2O

%C = 59.89%, %H = 6.2%

For $C_{10}H_{13}O_2Cl$,

%C = 60.0%, %H = 6.5%

/MOLECULAR.....

MOLECULAR WEIGHT

	Benzil	Benzil	Sub-stance
Weight of substance =	0.1230gm	0.1699gm	0.0950gm
Boiling point elevation =	1.052	1.456	0.836
Molecular weight found =	-	209.6	204.5

The molecular weight was determined cryoscopically using Menzies-Wright apparatus and benzene as solvent (see page 70). Benzil was used as the standard of comparison. For $C_{10}H_{13}O_2Cl$, the molecular weight is 200.5.

III. PREPARATION OF 1,3 ACETOXY-5-CHLOROMETHYL-2,4,6-TRIMETHYLRESORCINOL. (page 48)

0.5 gms 5-chloromethyl-2,4,6-trimethylresorcinol was suspended in 25 ml acetic anhydride. On adding two drops of concentrated sulphuric acid solution took place. The solution was left to stand overnight and then poured into 200 ml. water. An oil formed which crystallised on standing. The acetate was re-crystallised from water-acetone solution forming colourless needles. The yield was 60% and the melting point 135-7°C.

/PERCENTAGE.....

PERCENTAGE CHLORINE

0.2380 gms. substance produced 0.1197 gms. silver chloride.

$$\%Cl = 12.47\%$$

For 1,3-acetoxy-5-chloromethyl-2,4-6trimethylresorcinol, $C_{14}H_{17}O_4Cl$, %Cl = 12.47%.

MOLECULAR WEIGHT

The molecular weight was determined in the same way as for the previous compound except ethyl alcohol was used as the solvent.

	Benzil	Sub-stance	Sub-stance
Weight of subetance =	0.1906gm	0.1085gm	0.0676
Elevation of boiling point =	1.574	0.682	0.406
Molecular weight =	-	276	288.7

For $C_{14}H_{17}O_4Cl$ molecular weight = 284.5

MICROCOMBUSTION RESULTS

The analysis was performed by Weiler and Strauss (64). 3.954 mg. substance produced 8.475 mg.CO_2 and 1.960 mg. H_2O.

$$\%C = 58.46\%, \quad \%H = 6.9\%$$

For $C_{14}H_{17}O_4Cl$,

$$\%C = 58.96\%, \quad \%H = 6.0\%$$

From these results it was apparent that the new compound, 1,3-acetoxy-5-chloromethyl-2,4,6-trimethyl-resorcinol, had been prepared.

/ IV. .....

IV. PREPARATION OF 2,4,5,6-TETRAMETHYLRESORCINOL

(page 49)

(a) Attempted preparation

Finn and Musty (59) prepared tetramethylphenol in the following manner so it was considered that tetramethylresorcinol might possibly be made in the same way.

2 gms. 1,3-acetoxy-5-chloromethyl-2,4,6-trimethyl-resorcinol were dissolved in acetone in a small round-bottom flask fitted with a reflux condenser. Granulated zinc was added followed by 5 ml. concentrated hydrochloric acid. The reduction was allowed to proceed for six hours in the cold. Additions of 1 ml. of the acid were made when evolution of hydrogen ceased. The solution was raised to the boil, filtered and extracted with ether, most of which was evaporated off. The residue was refluxed with alcoholic sodium hydroxide (1 gm. in 10 gms. ethyl alcohol and water added until solution took place) for six hours. The solution was poured into 20 ml. water, acidified and steam distilled. ½ gm. product settled out. It was composed of colourless cubic crystals having a melting point of 205°C. It contained no chlorine.

/COMBUSTION.....

COMBUSTION RESULT

(1) 0.1578 gms substance produced 0.3797 gms CO_2 and 0.1150 gms H_2O.

%C = 65.61%, %H = 8.1%.

(2) 0.1550 gms substance produced 0.3689 gms CO_2 and 0.1066 gms H_2O.

%C = 64.9%, %H = 7.6%

Mean %C = 65.26%, %H = 7.9%

For tetramethyl resorcinol, $C_{10}H_{14}O_2$,

%C = 72.3%, %H = 8.4%.

It appears from these results that the substance was not tetramethylresorcinol. The latter has been prepared by Punzengruber and Bauer-Benedikt (63) who found that it had a melting point of 161.5 - 2°C. Obviously the required substance had not been produced.

(b) Preparation of Tetramethylresorcinol

A new method was devised for preparing tetramethylresorcinol.

1 gm. 5-chloromethyl-2,4,6-trimethylresorcinol was dissolved in 10 ml. ethyl alcohol and added to 5 gms zinc amalgam (prepared by adding 0.3 gm. mercuric chloride to 5 gms. zinc dust in the presence of dilute hydrochloric acid.) After shaking thoroughly the acid was decanted and the amalgam washed several times with

/water.....

water. 20 ml. dilute hydrochloric acid were added and the mixture heated on a water bath under reflux for 2½ hours. 2 ml. dilute hydrochloric acid were added every half hour. On cooling or reducing the volume of the solution by heating under vacuum, thick irregular colourless needles formed. The yield was 85%. The product was recrystallised from dilute alcohol or purified by vacuum sublimation. The melting point was 161-2°C. These properties agreed accurately with those obtained by Bauer-Benedikt and Funzengruber (63) for tetramethylresorcinol.

MICROCOMBUSTION RESULT

The microanalysis was performed by Weiler and Strauss (64).

3.510 mg. substance produced 9.280 mg. CO_2 and 2.605 mg. H_2O.

%C = 72.09%, %H = 8.2%

For 2,4,5,6-tetramethylresorcinol, $C_{10}H_{14}O_2$

%C = 72.3%, %H = 8.4%.

MOLECULAR WEIGHT

The molecular weight was performed using the Menzies-Wright apparatus, ethyl alcohol as solvent and benzil as the standard of comparison. (see page 79).

/Benzil....

	Benzil	Substance
Weight of substance =	0.1036 gm	0.0783 gm
Elevation of boiling point	0.796	0.744
Molecular weight		169.7

For 2,4,5,6-tetramethylresorcinol, $C_{10}H_{14}O_2$

Molecular weight = 166

(c) Another preparation of tetramethylresorcinol (page 51)

Tetramethylresorcinol was prepared in a second way using 5-hydroxymethyl-2,4,6-trimethylresorcinol as the starting material. The method used was exactly the same as described above.

After preparing the above mentioned alcohol it was not necessary to extract it from the water-dioxan mixture (see preparation of 5-hydroxymethyl-2,4,6-trimethylresorcinol). To the filtered solution of the resorcinyl alcohol, zinc amalgam and dilute hydrochloric acid were added. The solution was refluxed for 2½ hours. The tetramethylresorcinol was extracted in the same way as before.

B. DERIVATIVES OF TETRAMETHYLRESORCINOL (page 52).

(a) PREPARATION OF 1,3-ACETOXY-2,4,5,6-TRIMETHYL-RESORCINOL

½ gm. tetramethylresorcinol was dissolved in 15 ml. acetic anhydride and one drop of concentrated sulphuric

/acid.....

acid was added. The solution was left to stand overnight. It was poured into 200 ml. water when an oil separated out and crystallised on standing. The precipitate was recrystallised from acetone-water or alcohol-water solutions.

Colourless needles of melting point 98.5-99.5°C.

MICROCOMBUSTION RESULT

The analysis was performed by Weiler and Strauss (64). 4.010 mg. substance produced 9.895 mg. CO_2 and 2.600 mg. H_2O

%C = 67.3%, %H = 7.2%.

For 1,3-acetoxy-2,4,5,6-tetramethylresorcinol, $C_{14}H_{18}O_4$

%C = 67.2%, %H = 7.2%.

(b) The phenylurethane of tetramethylresorcinol

To 0.4. gm. tetramethylresorcinol was added 0.6 gm phenyl-iso-cyanate. The mixture was heated in a fume cupboard over a water bath for twenty minutes. Solution took place and on further heating the solution turned solid. The reaction was left overnight to complete in the cold.

The phenylurethane was very insoluble in water, so the precipitate was boiled a few times in water to remove excess tetramethylresorcinol and phenyl-iso-cyanate. The melting point of the white compound

/was.....

was 235-7°C.

MICROCOMBUSTION RESULT

The microcombustion was carried out by Weiler and Strauss (64).

4.144 mg. substance produced 10.755 mg. CO_2 and 2.210 mg. H_2O.

%C = 70.78%, %H = 5.9%

For the diphenylurethane derivative of tetramethylresorcinol, $C_{24}H_{24}O_4N_2$,

%C = 71.3%, %H = 5.9%

NITROGEN ESTIMATION

0.02165 gm. substance produced 1.41 ccs. nitrogen at 71.32 cms. mercury pressure and 15.5°C.

%N = 7.1%

Theoretical %N = 6.9%

V. 5-HYDROXYMETHYL-2,4,6-TRIMETHYLRESORCINOL (page 54)

(a) Attempted preparation

1 gm. 5-chloromethyl-2,4,6-trimethylresorcinol was shaken up with 40 ml. absolute alcohol. The substance was slightly soluble. 3 gm. silver oxide, freshly prepared by adding silver nitrate to sodium hydroxide, were added. The solution was then placed on a shaker for ten hours. After heating to boiling point, the solution was filtered and the ethyl alcohol

/evaporated.

evaporated. A red gummy material was obtained which would not recrystallise. This method of preparation was unsuccessful so it was abandoned.

(b) Preparation

The method used by Finn and Musty (59) to hydrolyse chloromethyl mesitol was followed.

2 gms. 5-chloromethyl-2,4,6-trimethylresorcinol were dissolved in 22 ml. dioxan, 10 ml. water were added and a few marble chips and the solution refluxed on a water bath for 6 hours and then filtered.

When the marble chips were added to the hot solution an immediate vigorous evolution of gas occurred on the chips.

When the solution was not either colourless or faintly yellow,it was steam distilled to remove dioxan, then clarified with animal charcoal followed by the reduction in volume by heating under vacuum. When the colour of the solution was either colourless or faintly yellow, it was not necessary to clarify with animal charcoal.

When precipitation did not result during vacuum distillation, it was necessary to leave it to stand for a few days. The addition of a little ether induced precipitation.

/Attempts.....

Attempts to recrystallise the compound failed. It was soluble in most organic solvents and insoluble in cold water, but, on dissolving in hot water, it did not recrystallise on cooling.

It was found that, when carefully prepared, the compound was pure white and amorphous. The melting point was 180-1°C. A mixed melt with the compound described in page 86 viz. the compound prepared by the condensation of mesorcinol with formaldehyde in alkaline medium, produced a depression of 2°C. indicating that these two compounds were the same.

A yield of 50% was obtained.

MICROCOMBUSTION RESULT

The microcombustion was carried out by Weiler and Strauss (64).

4.376 mgs. substance produced 9.900 mgs. CO_2 and 2.900 mgs. H_2O.

%C = 61.69, %H = 7.4%.

For 5-hydroxymethyl-2,4,6-trimethylresorcinol, $C_{10}H_{14}O_3$,

%C = 65.93%, %H = 7.7%.

It will be observed that the percentage carbon obtained in the microcombustion result is low. However the microcombustion results obtained for derivatives of this compound establish that the compound just

/described.....

described is 5-hydroxymethyl-2,4,6-trimethylresorcinol. The molecular weight determination also confirms the structure of this compound.

MOLECULAR WEIGHT

The molecular weight of the substance was determined as before by the elevation of the boiling point of ethanol using the Menzies-Wright apparatus and benzil as the standard of comparison. (see page 79)

	Benzil	Benzil	Substance
Weight of substance	0.1333 g.	0.1367g.	0.1089
Elevation of boiling point	0.554	0.562	0.518
Molecular weight			181.5

For 5-hydroxymethyl-2,4,6-trimethylresorcinol, $C_{10}H_{14}O_3$ molecular weight 182.

(c) RECONVERSION TO 5-CHLOROMETHYL-2,4,6-TRIMETHYL-RESORCINOL

0.2 gms. 5-hydroxymethyl-2,4,6-trimethylresorcinol was dissolved in ethyl acetate and added to a mixture of sulphuric and hydrochloric acids (2:1). An immediate precipitate of fine needles formed. A mixed melt with 5-chloromethyl-2,4,6-trimethylresorcinol gave no depression indicating that 5-hydroxymethyl-2,4,6-trimethylresorcinol had been reconverted to the chloromethyl derivative.

/PREPARATION.....

PREPARATION OF DERIVATIVES OF 5-HYDROXYMETHYL-2,4,6-TRIMETHYLRESORCINOL (page 56)

(d) (1) Preparation of the acetate

½ gm of the alcohol was added to 25 ml acetic anhydride. On heating gently, solution took place. ½ gm anhydrous potassium carbonate was added slowly, as fairly violent bubbling took place. The mixture was left to stand overnight and then dissolved in 150 ml. water. The derivative which remained undissolved was filtered off and recrystallised from 1:2 acetone-water solution. Colourless clusters of needles were formed in a yield of 70%. The melting point was 118-119°C.

MICROCOMBUSTION RESULT

The microcombustion was performed by Weiler and Strauss (64).

3.841 mg substance produced 8.770 mg CO_2 and 2.190 mg H_2O.

%C = 62.3%, %H = 6.3%

For 1,3-acetoxy-5-acetoxymethyl-2,4,6-trimethylresorcinol, $C_{16}H_{20}O_6$,

%C = 62.3%, %H = 6.5%

MOLECULAR WEIGHT

The molecular weight was determined from the

/elevation.....

elevation of the boiling point of ethyl alcohol using the Menzies-Wright apparatus and benzil as the standard of comparison (see page 79)

		Benzil	Substance
Weight of substance	=	0.1289 gm.	0.0886 gm.
Elevation of boiling point		0.546	0.252
Molecular weight	=		311

For 1-3-acetoxy-5-acetoxymethyl-2,4,6-trimethylresorcinol, $C_{16}H_{20}O_6$,
Molecular weight = 308

(d) (ii) Attempted preparation of the acetate

An attempt was made to prepare the acetate from 1,3-acetoxy-5-chloromethyl-2,4,6-trimethylresorcinol by reaction with silver acetate.

1 gm. of the chloromethyl compound dissolved in 40 ml. absolute alcohol on heating. 1 gm. silver acetate was added to 25 ml. water and 10 ml. glacial acetic acid. The silver salt was not entirely soluble. The latter was added to the alcohol solution and heated. The flask was corked and put on a shaker for three successive days.

Excess hydrochloric acid was added to form silver chloride with the excess silver acetate. The solution was boiled and filtered, and the filtrate vacuum distilled.

/A.....

A precipitate consisting mainly of a brown gum was obtained. On recrystallising from water-acetone solution, a very small quantity of colourless needles with a melting point of 106-8°C. was obtained. The Beilstein test for halogens was negative thereby indicating that the compound had lost its chlorine. Because of the very poor yield and the extravagant use of silver acetate, this experiment was not fully investigated.

(e) Preparation of the triphenylurethane derivative

0.4 gms. of the alcohol was added to 0.9 gms. phenyl-isocyanate. Solution was brought about by heating over a flame for ten minutes. On cooling the resulting liquid set to a solid mass. This was left to stand overnight.

The derivative was insoluble in water or ethanol. It was washed several times with hot ethanol. A fine white powder was obtained with a melting point of 224-5°C

MICROCOMBUSTION RESULT

The microcombustion was carried out by Messrs Weiler and Strauss (64).

3.399 mg. substance produced 8.565 mg. CO_2 and 1.62 mg H_2O.

/C.....

%C = 68.7%, %H = 5.3%

For the triphenyl urethane derivative of 5-hydroxymethyl-2,4,6-trimethylresorcinol, $C_{31}H_{29}O_6N_3$,

%C = 69.0%, %H = 5.4%

NITROGEN ESTIMATION

0.02091 gms. substance gave 1.45 ccs. nitrogen at 17.2°C. and 71.95 cms mercury pressure.

%N = 7.6 %

Theoretical %N = 7.8%

VI. 1:1'-3:3'-TETRAHYDROXY-2:2'-4:4'-6:6'-HEXAMETHYL-DIPHENYLMETHANE (page 58)

(a) Preparation

Difficulty was experienced in preparing a pure sample of this compound, but, finally, the following method proved to be the best:

1 gm. mesorcinol was dissolved in 2 ml. ethyl alcohol and 0.7 ml. formalin added. The solution was heated to boiling point and concentrated hydrochloric acid added drop by drop whilst heating was maintained. A brown oil gradually formed, and, when 0.7 ml. concentrated hydrochloric acid had been added, the solution was boiled for five minutes and then allowed to cool. The oil solidified to a brown precipitate and was filtered off. The precipitate was boiled in about 10 ml. water so as to remove any

/unreacted ...

unreacted mesorcinol, and the solution filtered hot. The remaining brown compound was recrystallised three times from dilute ethanol, when brown rod-like needles crystallised out. The melting point was 229-231°C.

MICROCOMBUSTION RESULT

The microcombustion was performed by Weiler and Strauss (64).

4.163 mg substance produced 10.530 mg. CO_2 and 2.900 mg. H_2O.

%C = 68.97%, %H = 7.7%

For 1:1'-3:3'-tetrahydroxy-2:2'-4:4'-6:6'-hexamethyl-diphenylmethane, $C_{19}H_{24}O_4$,

%C = 72.1%, %H = 7.6%

It will be observed that the percentage carbon found by experiment is lower than the theoretical amount. From the microcombustion result of the acetate and the molecular weight determination, however, it is obvious that the diphenylmethane compound had been prepared.

MOLECULAR WEIGHT

The molecular weight was determined by the boiling point elevation using the Menzies-Wright apparatus with ethanol as the solvent and benzil as the standard of comparison. (see page 79)

/Benzil...

	Benzil	Substance
Weight of substance	0.2197 gm	0.1297 gm
Elevation of boiling point	0.902	0.360
Molecular weight		310.7

For the diphenylmethane compound, $C_{19}H_{24}O_4$, molecular weight = 316

DERIVATIVES OF 1:1'-3:3'-TETRAHYDROXY-2:2'-4:4'-6:6'-HEXAMETHYLDIPHENYLMETHANE (page 59)

(b) Preparation of the acetate

½ gm of the diphenylmethane compound was dissolved in 15 ml. acetic anhydride and anhydrous potassium carbonate added slowly. Vigorous bubbling took place and the mixture was left overnight. It set hard. Excess water was added which dissolved all but a white precipitate. The precipitate was filtered and recrystallised twice from dilute alcohol. The melting point was 185-7°C.

MICROCOMBUSTION RESULT

The microcombustion was carried out by Weiler and Strauss. (69)

4.050 mg. substance produced 9.850 mg. CO_2 and 2.390 mg. H_2O.

/%C.....

%C = 66.3%, %H = 6.5%

For 1:1'-3:3'-tetracetoxy-2:2'-4:4'-6:6'-hexamethyl-diphenylmethane, $C_{27}H_{32}O_8$,

%C = 66.9%, %H = 6.6%.

(c) Preparation of the tetraphenyl urethane derivative

0.3 gm of the diphenylmethane compound was added to 0.5 gm phenyl-isocyanate and the mixture was heated on a water bath for 15 minutes when solution took place. On further heating, a precipitate formed and, on cooling, the whole mass solidified and was left overnight. It dissolved in dioxan and an oil was expelled on adding water. Even after drying, this oil did not crystallise. The original sample of the diphenylmethane used was not pure enough. Shortage of time and material did not permit further investigation.

VII. REACTION OF 2,4,6-TRIMETHYLRESORCINOL WITH 5-HYDROXYMETHYL-2,4,6-TRIMETHYLRESORCINOL (page 61)

(a) Under alkaline conditions

0.5 gms 5-hydroxy-2,4,6-trimethylresorcinol and 0.4 gm mesorcinol were dissolved in 20 ml 1% sodium hydroxide and the solution heated for two hours on a water bath. On neutralisation with dilute acetic acid, a very fine precipitate formed which coagulated to a gum. It dissolved in alcohol. On adding water, the

/solution.....

solution became cloudy, and a brown precipitate settled out on standing. The solution was filtered and the precipitate washed thoroughly with water. The melting point was 130°C. When the precipitate was boiled in water, a small quantity of a brown material remained, which also had a melting point of 130°C. It was therefore, apparent that the diphenylmethane derivative, which is insoluble in water and has a melting point of 230°C, had not formed.

It appears that no reaction takes place between these two compounds under alkaline conditions.

(b) Under acid conditions

0.5 gms. 5-hydroxymethyl-2,4,6-trimethylresorcinol and 0.4 gm. mesorcinol were dissolved in 5 ml. ethanol and 2 ml. dilute hydrochloric acid added. On heating, the solution turned red. The solution was refluxed for two hours on a water bath. On cooling, a precipitate settled. This was filtered in order to get rid of unreacted material, boiled in water. The hot solution was filtered leaving a brown precipitate which was recrystallised from dilute ethanol. The resulting brown needles had a melting point of 227-9°C. A mixed melt with 1:1'-3:3'-tetrahydroxy-2:2'-4:4'-6:6'-hexamethyldiphenylmethane gave a melting point of 226-8°C.,

/indicating.....

indicating that the 5-hydroxymethyl-2,4,6-trimethyl-resorcinol had condensed with resorcinol.

VIII. REACTION OF 5-HYDROXYMETHYL-2,4,6-TRIMETHYL-RESORCINOL WITH RESORCINOL. (page 62)

(a) In alkaline medium

Equal weights of the two compounds were dissolved in sodium hydroxide. The solution turned dark green. It was left overnight and then acidified with dilute acetic acid. The solution turned red. No precipitate formed, even on standing for 8 hours. The solution was extracted with ether. The ether layer was separated and the ether evaporated off. There remained a red oil which partially crystallised after standing for three days.

(b) Under acid conditions

Equal weights of the two compounds were dissolved in ethanol and concentrated hydrochloric acid added. The solution turned red, but no precipitate formed. The solution was extracted with ether. When the ether was evaporated off, there remained a red oil, which partially crystallised after standing for three days.

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