ATTEMPTED SYNTHESIS OF A
β- OR γ-
RESORCINYL ALCOHOL

by

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GRAHAMSTOWN.
1951

A Thesis submitted in fulfilment of the Requirements of the University of Rhodes for the Degree of Master of Science.

FOREWORD

The work described in this thesis was carried out under the direction of Dr. G. E. Little, M.A., to whom the author wishes to place on record his gratitude.

He also wishes to thank Professor W. F. Barker, B.Sc., Ph.D., F.R.I.C., for his interest in the work, Dr. J. A. Gledhill, M.Sc., for his assistance in glassblowing and Dr. F. G. van der Riet, M.A., A.B.L.S., for his help in obtaining sundry journals.

Finally, he wishes to acknowledge his indebtedness to the South African Council of Scientific and Industrial Research and the Southern Rhodesian Government for financial assistance received by him over the period of research.

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

CONTENTS

1. HISTORICAL

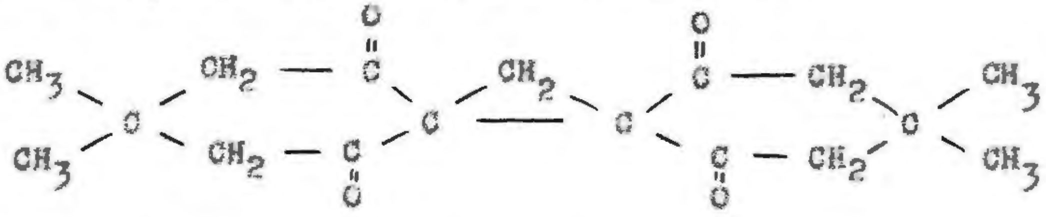
The ultimate objective of this research is the elucidation of the mechanism of the resorcinol-formaldehyde condensation. Whilst a vast literature has been built up about the phenol-formaldehyde condensation, that of resorcinol has received but scant attention, probably because the high reactivity of resorcinol rendered the following of the condensation extremely difficult.

The earliest observation concerning the resorcinol-formaldehyde condensation was due to Baeyer (1) who, in 1872, condensed resorcinol with various aldehydes. When the aldehyde was relatively inactive crystalline compounds were obtained but with acetaldehyde or formaldehyde a resinous product resulted. In 1892 Caro (2) condensed an excess of resorcinol with formaldehyde in the presence of dilute hydrochloric acid; the product obtained recrystallised from alcohol as white microscopic crystals, decomposed without melting at 250° and was stated to be bis (2-4 dihydroxy-phenyl) methane.

Möhlan and Koch (3) confirmed Caro's results.

In 1894 Merling (4) prepared a methylene bis derivative of dihydroresorcinol which led on to the important study of the condensation of 5-5 dimethyldihydroresorcinol (methone) with formaldehyde. (5,6). Methone reacted readily with formaldehyde to form methylene bis-methone and so sensitive was this reaction (7) that it was developed by Vorlander (8,9) and more recently by Weinberger (10) for the quantitative analysis of aldehydes.

Radulescu and Georgescu (11)developed a general method for the synthesis of poly-spirans and as an example the formation of cyclopropane bis (dimethyldihydroresorcinol) dispiran will be considered. These authors condensed 5-5 dimethyldihydroresorcinol with formaldehyde to form the methylene bis-methone which on being treated with sodium ethoxide in absolute alcohol yielded a sodium salt. This salt was suspended in absolute ether, agitated with 2 gram atoms of iodine and the required dispiran was obtained, i.e.



Similarly cyclopropane bis (phenyl dihydroresorcinol) dispiran was prepared from methylene bis phenyl dihydroresorcinol.

In 1925 Sen and Sarkar (12) claimed they had synthesised o-p dihydroxy benzyl alcohol but Boehm and Parlasia (14) were unable to repeat the work. The latter were able to prepare 3-5 dihydroxybenzyl alcohol.

From this time on, no studies were made on the structure of the resins from polyhydric phenols until von Euler and his associates included this type of condensation product in their work. (15,16). No claim was made as to the synthesis of a resorcinyl alcohol.

The kinetics of the condensation of resorcinol has been followed by Engeldinger (18), Dubrisay and Papault (19), and Little and Pepper (20). Evidence was obtained that the condensation was catalysed by both hydrogen and hydroxyl ions, but no evidence as to the nature of the product was adduced.

In recent years the condensation of resorcinol and formaldehyde has become of technical importance in the manufacture of adhesives, (21, 22, 23, 24), laminar material (22, 23, 26) and new resins (25, 27, 28). Hence it would appear to be of some interest to ascribe the nature of the condensation.

In deciding upon the most suitable lines of attack it would seem that a survey of the literature relating to the phenol-formaldehyde condensation, which might be expected to be closely related to that of resorcinol, would be of value.

2. REVIEW OF THE LITERATURE RELATING TO THE PHENOL-FORMALDEHYDE CONDENSATION

NATURE AND CHARACTERISTICS OF THE PHENOL-FORMALDEHYDE REACTIONS

The general character of phenol-aldehyde reactions was probably first recognised by Baeyer (1) in 1872. Baeyer found that methylene acetate reacted with phenol in the presence of concentrated hydrochloric acid to form a colourless resin. Ter Meer (29) used methylal with certain phenols and likewise obtained condensed products of resinous character which were not further investigated. Following the commercial production of formaldehyde in 1890, Kleeberg (30), at the suggestion of Emil Fisher investigated its reaction with phenol and published the results in 1891. Kleeberg found that formaldehyde reacted energetically with phenol, resorcinol and pyrogallic acid in the presence of concentrated hydrochloric acid to yield products which were insoluble in alkalies and were so difficult to purify that their composition could not be determined.

Hosaeus (31) referred to the unpublished investigations carried out by Tollens, who heated dilute formaldehyde solutions with phenol, resorcinol, pyrogallol and phloroglucinol with the addition of sulphuric or hydrochloric acid. In all cases resinous products separated which were either difficultly soluble or insoluble in all common solvents.

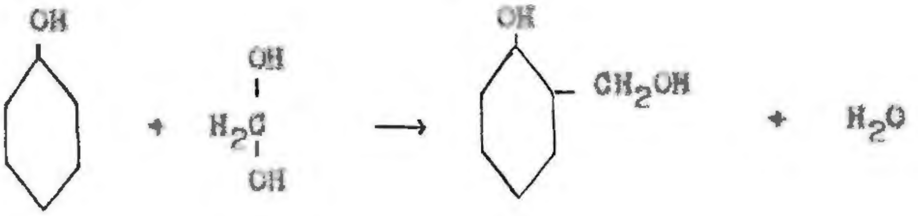
Commercial applications of phenol-formaldehyde resins were developed in the first decade of the twentieth century. In the latter part of this decade, Baekeland discovered a technique for moulding these resins. This work, together with that of Redman and other investigators, led to the development of the present phenolic resin industry.

In general, phenols reacted readily with formaldehyde in the presence of both alkaline or acidic catalysts, producing a variety of substances ranging from the simple methylol and methylene derivatives to the complex resins in which a large number of phenolic molecules were linked together by methylene groups.

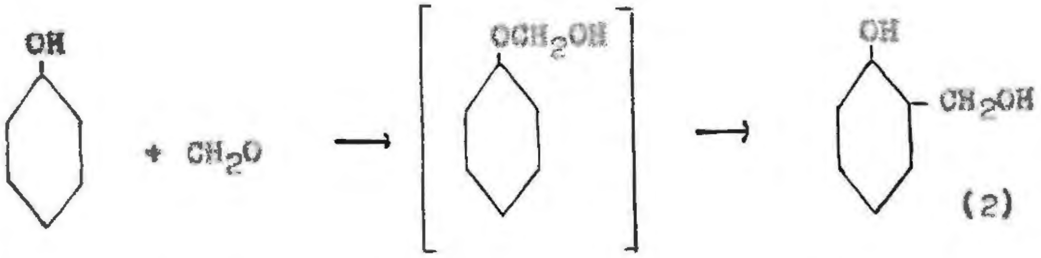
The reactivity of the ortho and para hydrogen atoms in the phenolic nucleus was the predominant factor in phenol-formaldehyde reactions. Although there was some indication that the meta hydrogen atoms might become involved when other positions were blocked, as yet, this had not been conclusively demonstrated. Nuclear derivatives were the principal reaction products and formals, such as were obtained from alcohols and formaldehyde, were never isolated.

The two most important phenol-formaldehyde reactions were found to be: (A) the formation of nuclear methylol phenols or phenol alcohols, as they are commonly designated and (B) the formation of polynuclear methylene derivatives.

The production of a phenol alcohol may be illustrated by the formation of o-hydroxybenzylalcohol (saligenin). The mechanism of the addition of formaldehyde is not entirely understood. Manasse (13) suggested that the formaldehyde might react in alkali solution as methylene glycol as indicated in equation (1) or it might undergo an acetal addition, with the subsequent rearrangement of the hemiformal as was suggested by von Tollens and later by Baekeland and Bender (32). This mechanism was represented by equation (2)

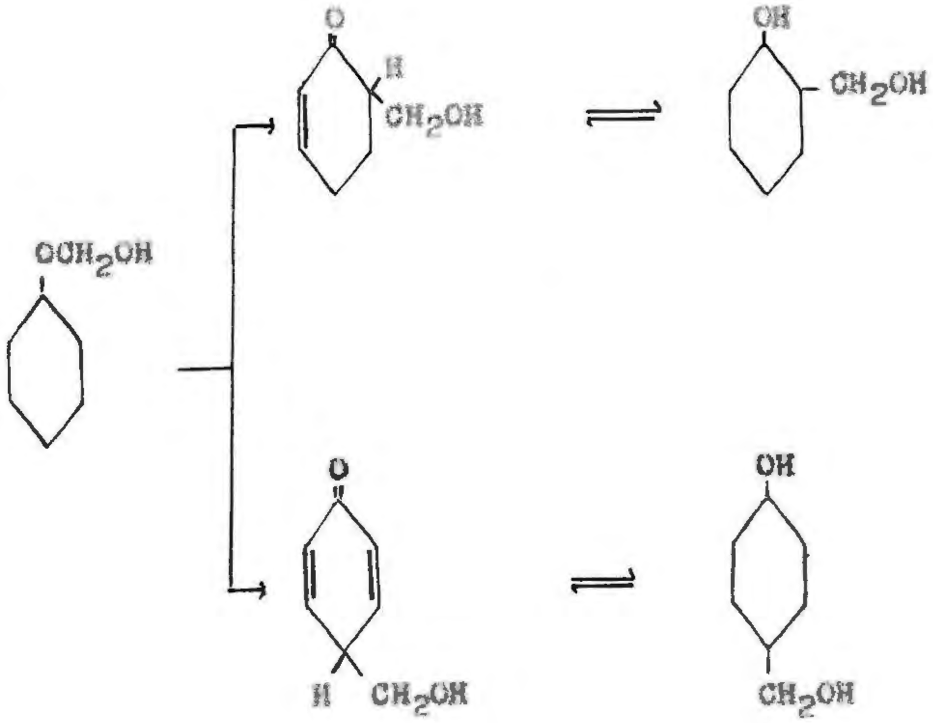


(1)



(2)

Walker (33) favoured the idea of the formation of a primary phenolic hemiformal and suggested that the formation of the phenol alcohols might involve tantomeric rearrangement of the type indicated below:

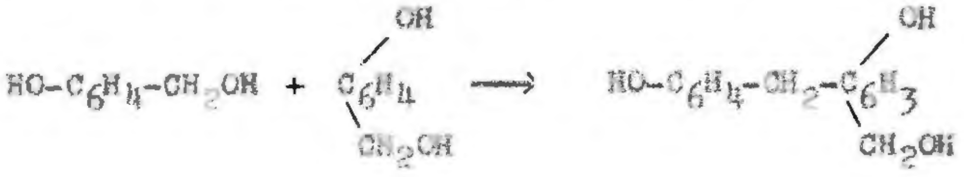


Nuclear methylene derivatives were apparently formed by a secondary reaction and Raschig (34) suggested that the phenol alcohols might react in two ways:-

(1) with more phenol to give diphenylmethanes

$$HO-C_6H_4-CH_2OH + C_6H_5OH \longrightarrow HO-C_6H_4-CH_2-C_6H_4OH$$

(2) with themselves to form alcohols of diphenylmethanes



$$HO-C_6H_4-CH_2OH + \underset{CH_2OH}{\overset{OH}{C_6H_4}} \longrightarrow HO-C_6H_4-CH_2-\underset{CH_2OH}{\overset{OH}{C_6H_3}}$$

Resin formation resulted from reactions of this type in which a number of mono- or poly-methylol phenol molecules condensed to form resitols, which were macromolecules only partly united by methylene groups and resites, which were branched-chain molecules.

FORMALDEHYDE CONDENSATIONS WITH PHENOL AND ITS HOMOLOGUES

A number of specific examples will be recorded.

(a) SALIGENIN AND POLYMETHYLOL PHENOLS.

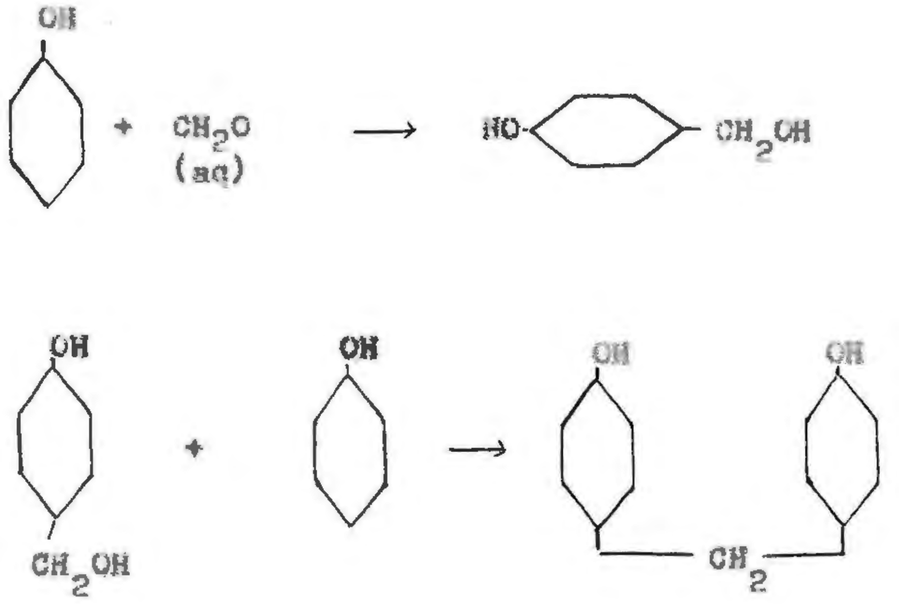
The preparation and isolation of phenol alcohol was first accomplished by two independent investigators, Manasse (13) and Lederer (35), who employed processes involving basic catalysis. Lederer's procedure involved the use of heat in the presence of milk of lime or baryta water, whereas Manasse favoured the employment of an approximately equimolar amount of strong alkali and the reaction was allowed to take place at room temperature. The latter method has been generally adopted as the standard procedure for phenol alcohol preparations. Saligenin was synthesised by Manasse's method. Phenol was dissolved in somewhat more than an equivalent amount of dilute caustic soda solution. An equivalent amount of formaldehyde (40% aqueous solution) was added and the mixture was allowed to stand until the odour of formaldehyde disappeared.

Then the solution was neutralised with acetic acid and extracted with ether to remove the phenol alcohols and uncombined phenol. The latter was removed by steam distillation and from the crude product saligenin was separated by extracting with benzene at 50°C. von Auwers and Daecke (36) observed that p-hydroxy benzyl alcohol which cannot be purified, resinified on standing.

Granger (37) carried out an extensive investigation of the initial reaction products of phenol with formaldehyde in alkaline media and found that in all cases the first products formed were the phenol alcohols. It was suggested by von Auwers (38) and is now generally accepted, that formaldehyde reacted with phenol only in positions ortho and para to the hydroxy group. Therefore, two mono alcohols, two dialcohols and one trialcohol were theoretically possible. Granger's work indicated that all five of these compounds were formed.

So far the condensation of phenol with formaldehyde has been considered only in alkaline media and when condensation was carried out in acidic media the results obtained were very different. In 1892 Noelting and Herzberg (39) isolated a crystalline product from the resinous products obtained by reacting two moles of phenol and one of formaldehyde in the presence of very dilute hydrochloric acid. They identified the compound as 4-4' dihydroxy diphenyl methane. Fraubenberg (40) isolated an isomeric diphenyl methane derivative from a reaction mixture similar to that studied by Noelting and Herzberg. This isomeride was not identified by Fraubenberg and in 1930 Megson and Drummond (41) proved the isomeride to be 2-4' dihydroxy diphenyl methane. The 2-2' dihydroxy diphenyl methane was prepared recently by the reaction of phenol and formaldehyde in the presence of zinc oxide as catalyst. (58)

Since the formation of methylol derivatives as primary products even under acidic conditions has been definitely demonstrated (42), the reaction probably was:



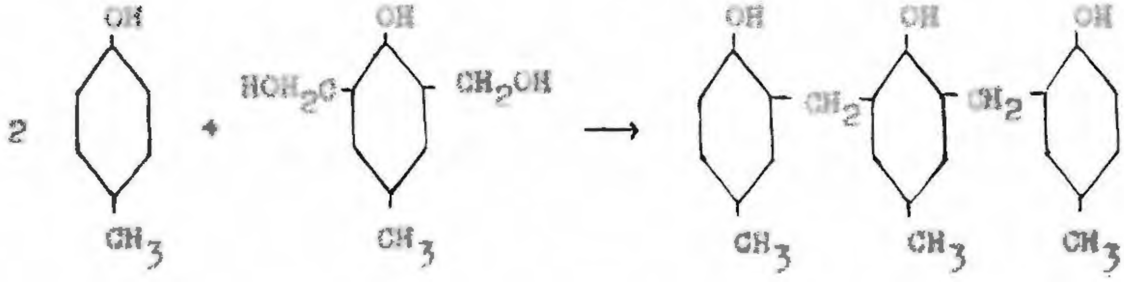
(b) CRESOLS.

The cresols, like phenol, gave the expected methylol derivatives with formaldehyde. Lederer (35) and Manasse (13) found that by using an alkaline medium p-cresol formed the monoalcohol, p-homosaligenin. The dialcohol, 2-6 dimethylol-p-cresol was prepared by Ullman and Brittner (43) by the reaction of one molecule of p-cresol on two molecules of formaldehyde, using sodium hydroxide as the catalyst. Megson and Drummond (41) synthesised 2-2' dihydroxy-5-5'-dimethyl diphenyl methane by reacting p-cresol with formaldehyde in an acidic medium.

The mono alcohols of o-cresol were difficult to prepare, since on reacting equimolar quantities of o-cresol and formaldehyde in the presence of alkali, the dialcohol was obtained as the principal product and a considerable quantity of unreacted cresol was recovered (37). Granger identified the dialcohol as 2-4 dimethylol-o-cresol. Under acidic conditions 4-4' dihydroxy-3-3'-dimethyl diphenyl methane was obtained. (41)

m-Cresol reacted readily with formaldehyde and the alcohols formed resinified rapidly even under alkaline conditions. As a result, the isolation of the pure phenol alcohol was extremely difficult. However, Megson and Drummond (41) obtained a crystalline product which they identified as 2-hydroxy-4-methyl benzyl alcohol. When an acidic catalyst was employed they obtained 4-4' dihydroxy-2-2' dimethyl diphenyl methane in a small yield.

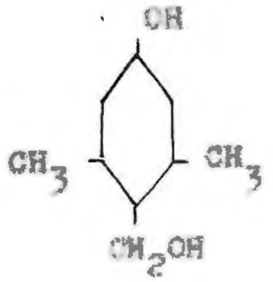
A rather important reaction of p-cresol was the isolation of a trinuclear methylenic derivative from the condensation products. (41,44). The structure of this compound was indicated by its synthesis which was carried out by reacting 2-6 dimethylol-p-cresol with excess p-cresol in the presence of hydrochloric acid. (44).



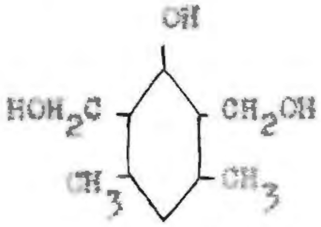
Niederl and McCoy (50) suggested that the compound was not a linear three nuclear compound but a cyclic four nuclear compound. However, Finn and Lewis (51) presented very strong evidence in support of the earlier trinuclear formulation.

(c) XYLENOLS.

In 1907 von Auwers (38) described the formation of a mono alcohol of 3-5 xylenol which he prepared under alkali conditions. He believed the substitution to be para to the hydroxy group. At the same time von Auwers isolated a small quantity of substance which he claimed to be an impure dialcohol. In 1934 a definite dialcohol was synthesised by Leighton Homes at the Chemical Research Laboratory, D.S.I.R., Teddington (unpublished works) through the interaction of 3-5 xylenol with formaldehyde in sodium ethoxide. Preliminary work by Megson indicated a probable ortho-ortho structure. This result was unexpected in view of von Auwer's structure for the mono alcohol because the latter would be expected to be intermediate in the formulation of the dialcohol. Finn, Lewis and Megson (45) proved that von Auwer's formula for the mono alcohol (i) was correct and that of the dialcohol (ii) was characterised as having an ortho-ortho structure.

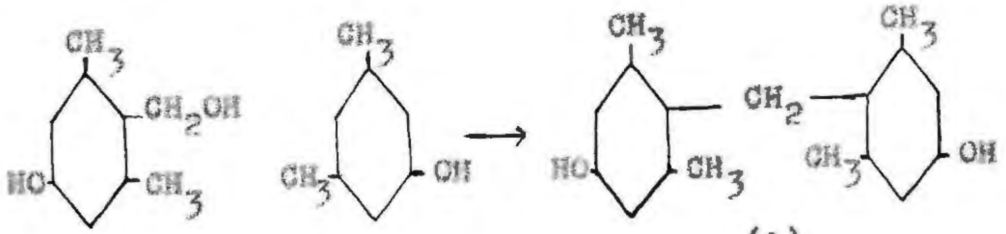


(i)

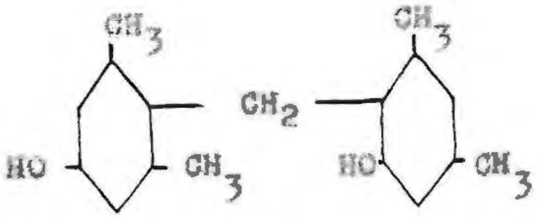


(ii)

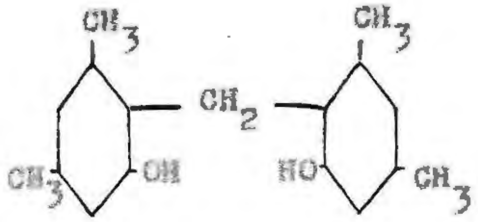
Morgan and Megson (46) have isolated all three isomerides from the acidic condensation of 3-5 xylenol, and have synthesised one of them from 3-5 xylenol alcohol and 3-5 xylenol.



(i)



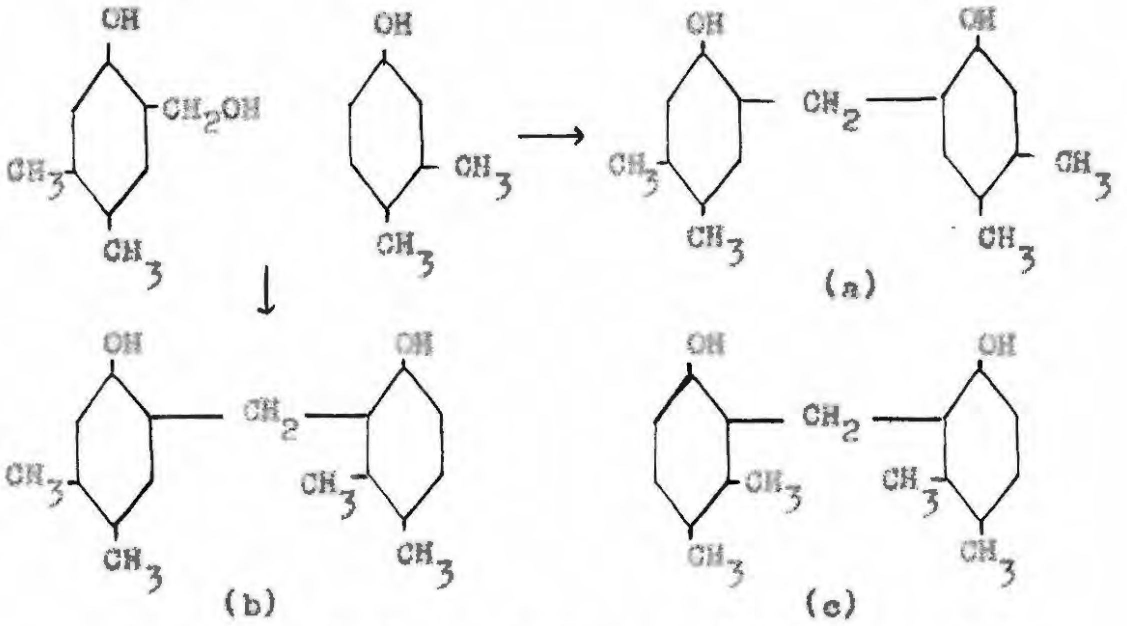
(ii)



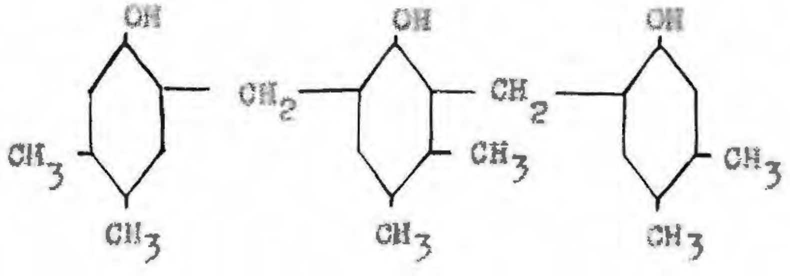
(iii)

Likewise in 1907, Fries and Kaun (47) formed the alcohol of 3-4 xylenol and under acidic conditions, Morgan and Megson (46) claimed that they had isolated

3 isomerides, two of which were synthesised and melting points recorded.



Recently, Ziegler and Zigeuner (48) obtained two compounds whose melting points were identical to those of two of Morgan and Megson's isomerides i.e. melting points 212-213°C. and 167°C. Ziegler and Zigeuner deduced that the compound melting at 212-213° had a trinuclear structure (d) while the other compound had the structure accorded to Morgan and Megson's (a).



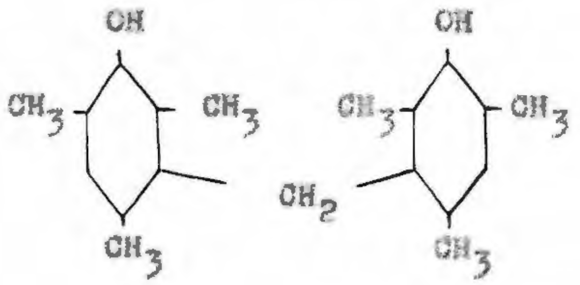
(d)

Similarly Usmani (49) prepared two compounds of melting point 167°C. and 212-213°C. by the action of heat on the mono alcohol of 3-4 xylenol.

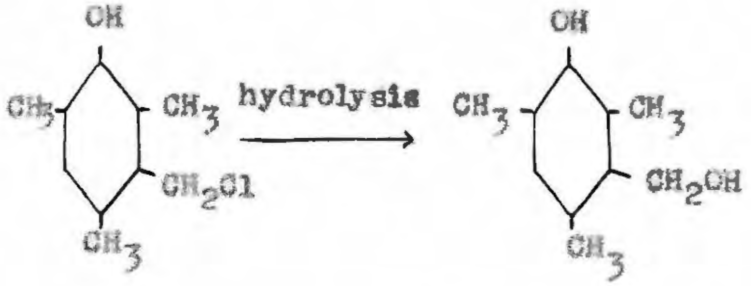
However, Finn (52) obtained specimens of the compound melting at 212-213° from Ziegler and Zigeuner, Morgan and Megson, and Usmani and by mixed melting point determinations proved the compounds to be identical. Also molecular weight determinations gave results corresponding closely to the theoretical value for a trinuclear compound. It was therefore confirmed that the compound (m.pt. 212-213°C.) first described by Megson and Morgan had in fact the trinuclear structure attributed to it by Ziegler and Zigeuner.

(d) MESITOL (2-4-6 TRIMETHYL PHENOL).

Mesitol, all of whose active nuclear positions are blocked, gave a crystalline methylene bis derivative when reacted with formaldehyde under strongly acid conditions (53). Recent work by Finn and Musty (54) has elucidated the structure of the diphenyl methane derivative as:



Attempts to prepare the mono methylol derivative of mesitol by alkali condensation failed but it was prepared via the chloromethyl derivative which on hydrolysis in aqueous dioxane solution gave the required alcohol. (54).



(e) PHLOROGLUCINOL AND PYROGALLOL.

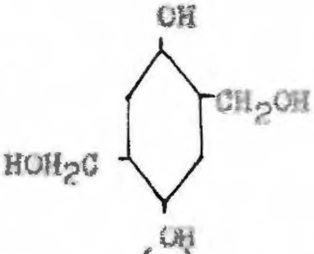
Hosaeus (31) obtained resinous products when he treated the above compounds with formaldehyde under acidic conditions. Boehm (55) was able to obtain a small quantity of symmetrical hexahydroxy diphenyl methane, together with more complicated products, by condensing phloroglucinol with formaldehyde in the presence of hydrochloric acid. These products of further condensation were apparently nuclear polymethylene derivatives, since on reduction of the crude acid condensation product with zinc dust and caustic soda, mono-, di- and tri-methyl phloroglucinol, as well as phloroglucinol itself were obtained.

Pyrogallol, on condensation with formaldehyde in a 10% hydrochloric acid solution, yielded the methylene derivative (2).

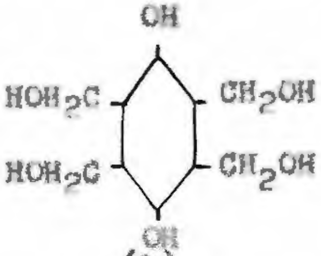
There appeared to be no references in which phloroglucinol and pyrogallol were condensed with formaldehyde in the presence of alkali but it has been proved that resin formation in polyhydric phenols went faster with the meta- compounds and pyrogallol. (25) Hence it would appear that these two compounds were as reactive as resorcinol in their condensation with formaldehyde.

(f) HYDROQUINONE AND CATECHOL.

In the case of hydroquinone it was shown that alkali condensation with two moles of formaldehyde gave a dialcohol (a), while four moles of formaldehyde gave a tetra alcohol (b)



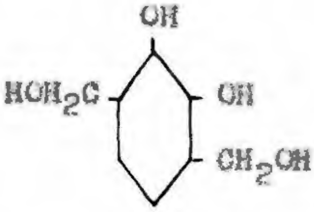
(a)



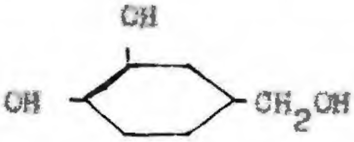
(b)

On treatment with an acid the dialcohol resinified to an insoluble amorphous product to which von Euler, Adler and Gie (15) ascribed a methylene bridge structure.

The alkali condensation of catechol with formaldehyde gave only catechol dialcohol in which the positions of the methylol groups were established by von Euler, Adler, Kispeizy and Fagerlund (16) to be



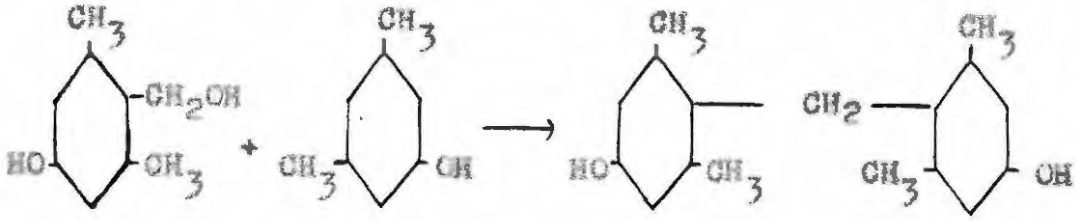
The catechol dialcohol resinified on heating. Rosenmund and Boehm (17) prepared the mono alcohol derivative by reduction of the corresponding aldehyde i.e.



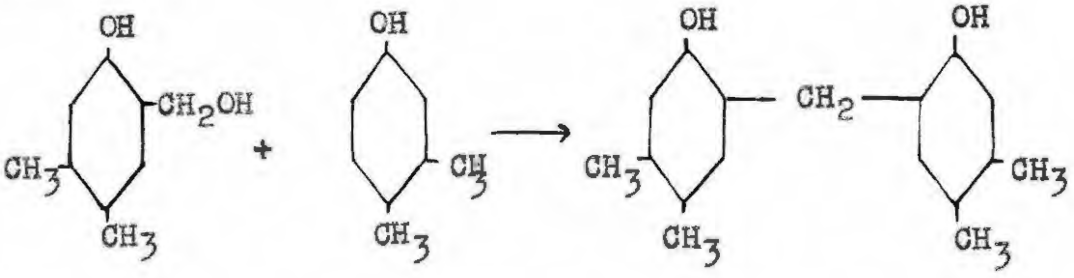
THE EFFECT OF (a) ACIDS AND (b) HEAT ON METHYLOL DERIVATIVES

(a) Granger (42), Megson and Morgan (46) and Koebner (44) have all clearly shown that phenolic mono alcohols may function as intermediates even in acidic condensations, although they have been but rarely isolated during these reactions.

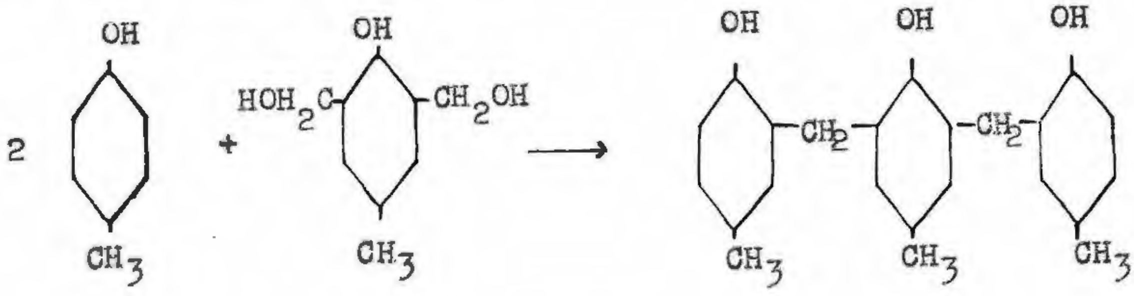
(i) Megson and Morgan (46) synthesised the methylene derivative of m-5-xylenol by condensing m-5-xylenol alcohol with m-5 xylenol in acidic media



Likewise, they were able to synthesise 2-2' dihydroxy-4-4'-5-5' tetramethyl diphenyl methane as follows:-

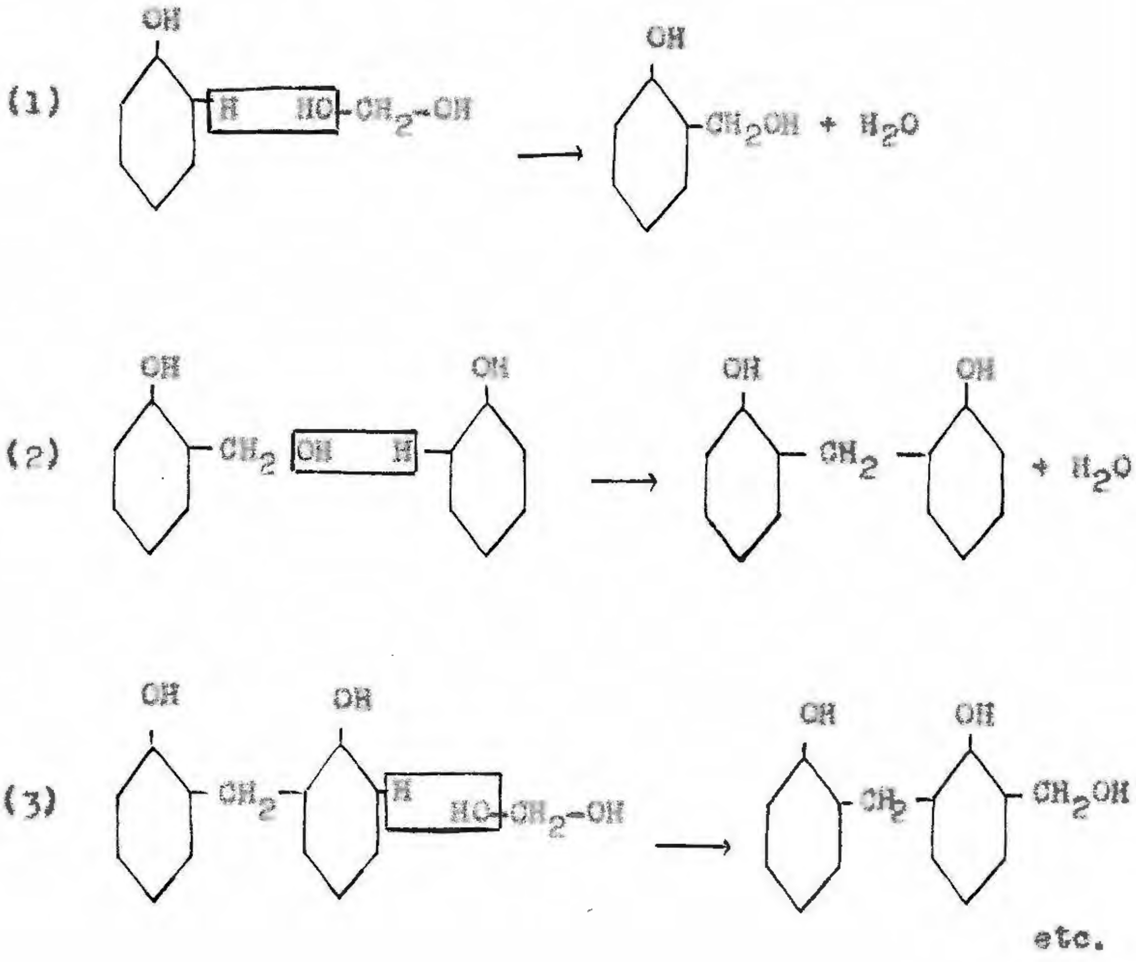


(ii) Koebner (44) synthesised the trinuclear derivative of p-cresol by the reaction of 2-6 dimethylol p-cresol with excess p-cresol in the presence of hydrochloric acid.



Koebner by condensing p-cresol with the appropriate methylol derivatives of dicresyl methane was able to isolate pure compounds with two, three, four and five cresyl rings.

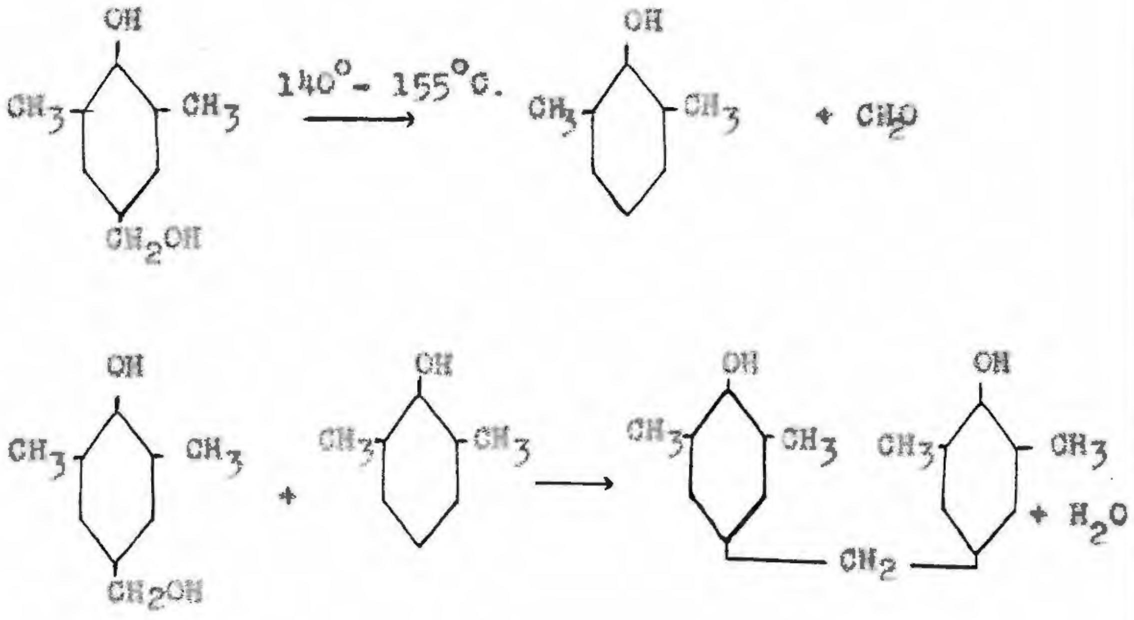
(iii) In 1946 Jones (56) studied the Kinetics and Thermochemistry of the phenol-formaldehyde reaction. Thermochemical studies showed that the heat evolved during the phenol-formaldehyde reaction could be regarded as derived from the reaction of formaldehyde with a phenolic molecule, and the subsequent elimination of water by condensation. In aqueous solution formaldehyde existed mainly as methylene glycol and Jones formulated the structure of a complex resin by this sequence.



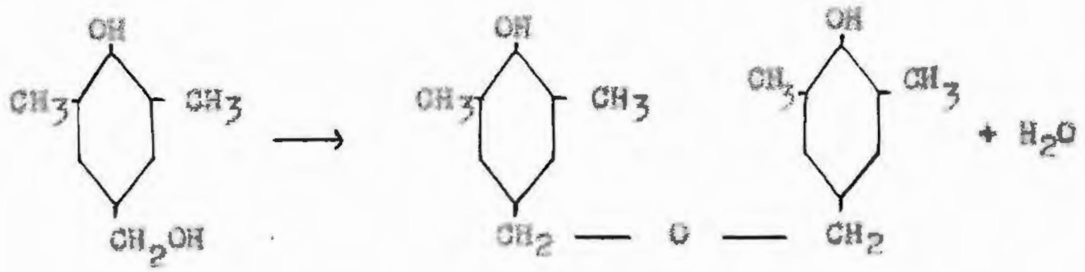
(b) The effect of heat on a phenol alcohol has been studied by von Euler, Adler, Cedwell and Törngren (57). When a phenol alcohol was heated, some formaldehyde was split off with the regeneration of the original phenol. The phenol then combined with the unchanged phenol alcohol, with the splitting out of water and a dihydroxy diphenyl methane derivative was formed. They were also able to isolate in the pure form dihydroxydibenzyl ether, phenol aldehyde, dihydroxystilbene, the dimer and trimer of methylenequinone and dihydroxydiphenylethane.

A typical reaction of this type is shown for 4-hydroxy-3,5-dimethylbenzyl alcohol.

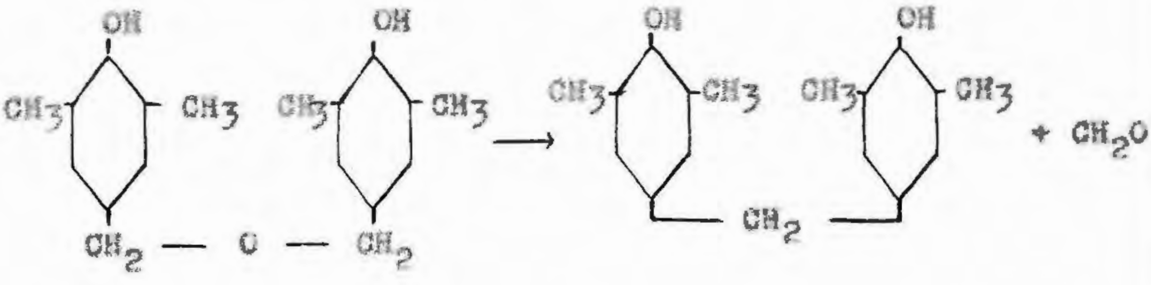
(i) Formation of the diphenyl methane derivative.



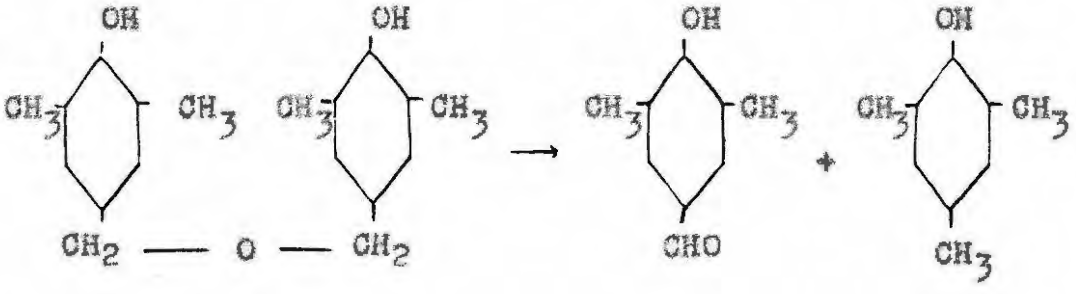
(ii) Formation of the dihydroxydibenzyl ether

2 

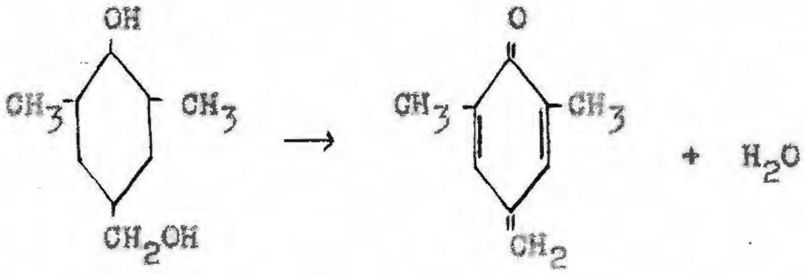
(iii) On further heating, particularly at temperatures higher than were needed to form the ether, the ether broke down to yield a dihydroxy diphenyl methane derivative and formaldehyde.



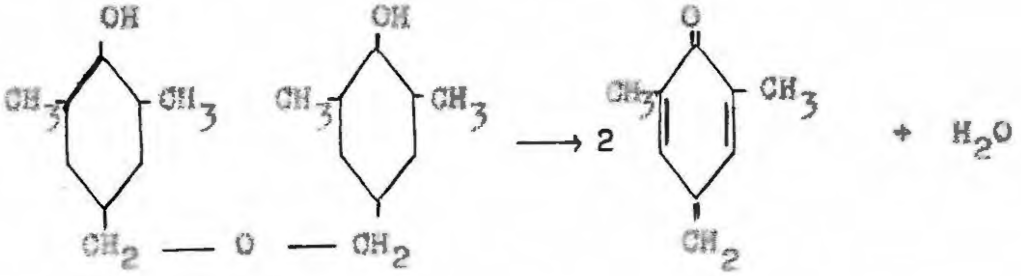
(iv) Small quantities of phenol aldehydes were usually found in the cured product. Zinke suggested that these were formed by the thermal cracking of the dihydroxydibenzyl ether. The yield of the aldehyde was small (4%) but for 3-5 dichloro-2-hydroxy benzyl alcohol, Zinke and Ziegler (59) obtained a considerable yield of aldehyde.



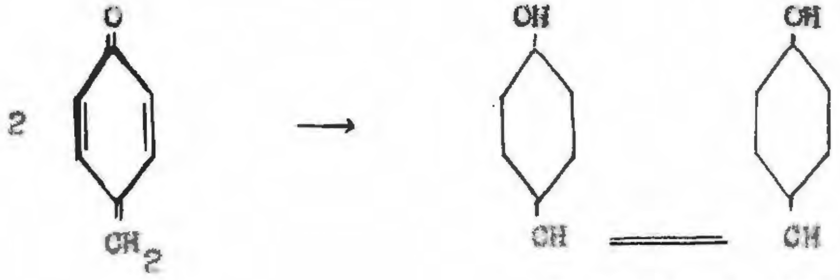
(v) Methylenequinone which was very reactive might be formed directly from the phenol alcohol by loss of water



or it might be formed by loss of water from the dihydroxydibenzyl ether.

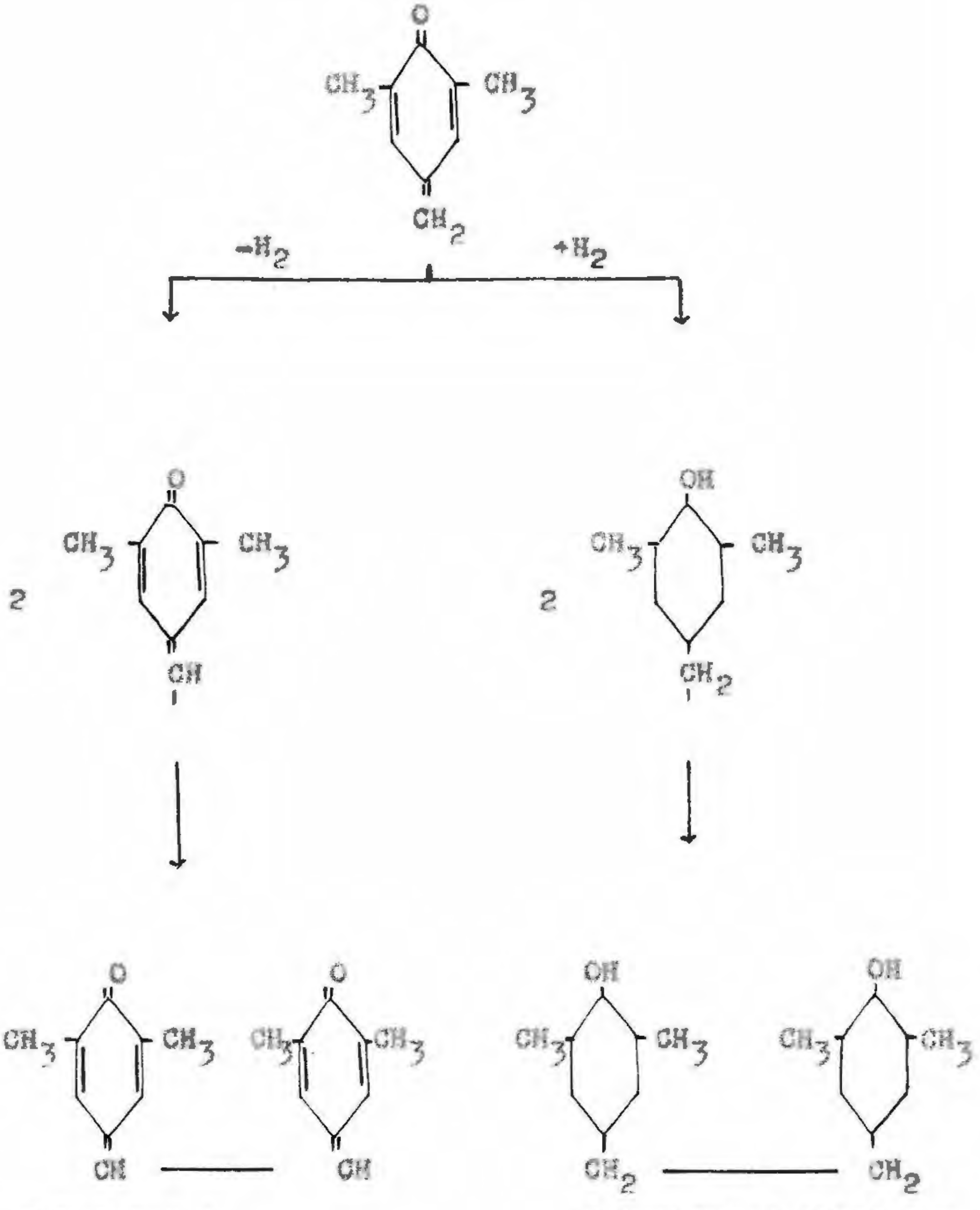


(vi) Methylenequinone was a very reactive and unstable compound and it might simply polymerise to form dihydroxydiphenyl ethane or dimerise to give dihydroxystilbene.



Dihydroxystilbene.

(vii) It was also possible that methylenequinone might undergo a direct disproportionation while in an unstable state and yielded radicals which became stabilised on the one hand to stilbenequinone and on the other to a diphenyl ethane.



Substituted Stilbenequinone.

Substituted dihydroxy diphenyl ethane.

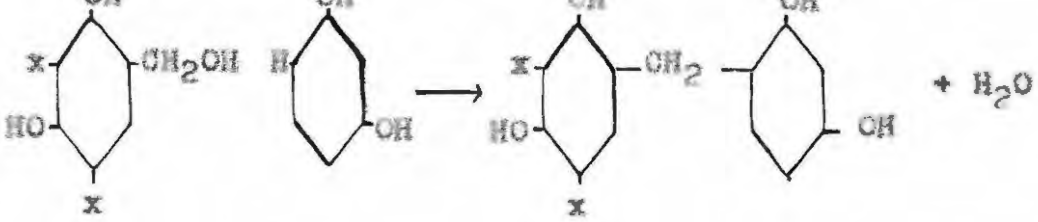
This series of reactions indicated what happened when a simple methylol derivative was heated and hence the curing of resols represented a complicated series of reactions.

Resols obtained by (i) condensing phenol with formaldehyde in the presence of alkali and (ii) the action of heat on the primary condensation product were fairly stable i.e. at room temperature they would take months before resinification would occur. Whereas those for resorcinol resinified rapidly and if it was assumed that the resorcinol-formaldehyde condensation was analagous to that of the phenol-formaldehyde condensation then it could be postulated that this difference in behaviour was due to the increased reactivity of the methylol groups. It was the aim of this thesis to synthesis a stable methylol derivative of a compound of resorcinol.

3. OUTLINE OF PRESENT RESEARCH.

Resorcinol, like phenol, has three reactive positions but the hydroxyl groups are meta to one another which causes the high reactivity of the resorcinol molecule (25). Up to the present the formation of a methylol derivative has failed and in all cases a resin has been obtained (14). Hence to restrict the condensation certain groups were introduced into two of the reactive positions leaving one at which condensation might take place. No references could be found in the literature concerning the successful preparation of a methylol derivative of this type. However, it was hoped that such a methylol derivative could be obtained which in turn would be condensed with resorcinol and from the structure of the resulting compound the mechanism of the condensation could be formulated.

e.g. Hypothetical



Three main methods were employed.

(1) To synthesise 2-4 or 4-6 disubstituted resorcinols and to examine their condensation with formaldehyde in order, if possible, to isolate the corresponding alcohol. In this case the position 6 or 2 was available for condensation.

(2) To chloromethylate a compound in which the substitution was such as to restrict the condensation to position 2 or 6. If formed the product could be readily hydrolysed to the alcohol.

(3) To reduce a suitably substituted aldehyde to the corresponding alcohol. The position of the aldehyde group had to be either 2 or 4 or 6.

(4) In addition the condensation of saligenin and resorcinol in the presence of alkaline and acidic catalysts was studied.

The main line of approach to the many problems associated with resin formation was an attempt to carry out a particular condensation under conditions as mild as possible, to eliminate the unchanged reactants, to isolate chemical compounds from the condensed residue and if possible to identify them. The difficulty of working with these condensed products was recognised by Baekeland (80) in 1911 who wrote:

"It should be pointed out that we have to deal here with substances which are amorphous, non crystalline, non volatile and cannot be purified in the usual ways. Furthermore, in any of these reactions, several substances are liable to be produced at the same time. These substances can form solid solutions one with another or with any excess of reacting material employed".

The difficulty of assigning structures to such compounds is obvious. Clearly elementary analysis will play a large part.

A. CONDENSATION OF SALIGENIN WITH RESORCINOL.

Saligenin was prepared by the catalytic reduction of salicylaldehyde (93).

Under acidic conditions and at room temperature saligenin condensed with resorcinol to give a thickish white precipitate which was recrystallised from ether and petroleum ether. On standing the compound darkened and had a melting point of 180°C. From microcombustion data the compound appeared to be 2-2'-4'-trihydroxy diphenyl methane and not the isomeride 2-2'-6' trihydroxy dibenzyl methane because the β position of the resorcinol molecule was very reactive (14). No reference to this compound could be found in the literature.

Attempts to react saligenin in the presence of alkali at (i) room temperature, (ii) 60°C. and (iii) 100°C. were unsuccessful. The mixture of reactants was separated by fractional crystallisation using benzene as the solvent. This was very difficult to bring about especially in the case of obtaining pure saligenin. However, it was shown that resorcinol did not condense with saligenin in the presence of alkali and also that saligenin did not condense with itself to form the dibenzyl ether or diphenyl methane derivative. Here, there was some support for Zinke and Ziegler (95) who stated that in the case of phenolic alcohols ether formation was retarded by the presence of alkali.

B. REACTION BETWEEN FORMALDEHYDE AND SUBSTITUTED RESORCINOLS.

I. 4-6 DIBROMORESORCINOL.

This compound was synthesised more successfully by Zehenter's method (60) than by Kohn and Löff's (62) and a modification of the former method was developed which gave a yield of 65%.

4-6 Dibromoresorcinol was condensed with 40% formalin using hydrochloric acid as catalyst and (i) absolute alcohol, (ii) glacial acetic acid and (iii) 40% formalin as solvent at 60°C. for three hours. The colour of the solution became yellowish brown with the formation of a brownish red precipitate which was filtered off. The filtrate was extracted with ether and no solid material was obtained.

The condensed products appeared to resemble one another and had the following characteristics. (1) They were very insoluble, (2) they did not melt, (3) they were amorphous. They appeared to be resins.

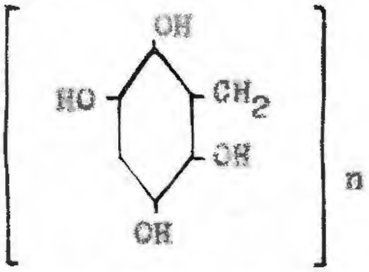
This method of preparation was far too drastic for the preparation of the required alcohol and the procedure was repeated at room temperature.

Under acidic conditions and at room temperature a brownish product was obtained which was insoluble in all common solvents except n-butanol from which it was recrystallised. The pure product was a brown amorphous powder which had no melting point.

Very little information was obtained from the combustion and halogen estimation results and the analysis figures were thus not helpful in ascribing a possible structure for this product. It had all the properties of a resin from which a certain amount of bromine had been removed.

On being condensed under alkaline conditions at room temperature, a brown coloured product was obtained. The purified compound was a brown, amorphous solid which did not melt.

From the analysis results all the bromine had been displaced. The product was very insoluble and was thought to be a Novolac type of resin having the unit:



where the bromines were displaced by hydroxyl groups.

In order to investigate the removal of bromine from 4-6 dibromoresorcinol, samples were treated with sodium hydroxide and 40% formalin respectively and the mixtures were allowed to stand for a week. In both cases halide ion was detected but to a greater extent in the former. Both the sodium hydroxide and 40% formalin were responsible for the removal of bromine.

From the reaction of sodium hydroxide on 4-6 dibromoresorcinol one could expect the formation of 1:2:4:5 tetrahydroxy benzene and as a matter of interest this course was investigated.

Mukerji (68) synthesised 1:2:4:5 tetrahydroxybenzene by a very laborious process which he summarised as follows:- resorcinol-dinitroresorcinol-diaminoresorcinol-dihydroxy-p-benzoquinone-tetrahydroxybenzene. The yield, reckoned on the weight of resorcinol taken, amounted to only 1-1.5%. If all the bromine atoms could be replaced by hydroxyl groups a new and easier method of synthesis for the said compound would have been accomplished. It was indeed very difficult to remove all the bromine and by considering the work of Jackson and Beggs (69), Nietzki and Schmidt (70), there was evidence for the presence of a very small quantity of 1:2:4:5 tetrahydroxybenzene.

From this result it appeared that it was the sodium hydroxide and formalin in conjunction which removed the bromine.

II. 5-NITRO-β-RESORCYLIC ACID.

This compound was prepared by the nitration of β-resorcylic acid.

β-Resorcylic acid was prepared by the action of potassium bicarbonate and carbon dioxide on resorcinol in aqueous solution and the potassium salt of the acid was hydrolysed with concentrated hydrochloric acid to give β-resorcylic acid. (71, 72).

Various methods of nitration were employed and the best method was found to be that of "Mixed Acids" i.e. concentrated nitric and sulphuric acids in the ratio of 2:1, in which a yield of 60% was obtained. The other methods employed were (i) a modified Parekh and Shah,(73) (ii) sodium nitrate and concentrated sulphuric acid and (iii) excess concentrated nitric acid.

On condensing with 40% formalin using both acid and alkali as catalyst, at room temperature and at 60°C. for four hours, the reaction failed to take place as was proved by mixed melts.

It was concluded that the presence of a nitro and carboxyl group deactivated the benzene nucleus to such an extent as to prevent the reaction from taking place.

III. 2-4 DINITRORESORCINOL.

2-4 Dinitroresorcinol was prepared by means of a two stage synthesis, (1) the synthesis of 2-4 dinitrosoresorcinol and (2) the oxidation of 2-4 dinitrosoresorcinol to 2-4 dinitroresorcinol.

2-4 Dinitrosoresorcinol was synthesised by either the Fitz's or Schultz's method (78). The former was found to give the best results. The 2-4 dinitrosoresorcinol was oxidised by using concentrated nitric acid, in accordance with Kostanecki and Feinstein (79).

No reaction took place when 2-4 dinitroresorcinol was condensed with 40% formalin under acidic and alkaline conditions, at room temperature and at 60°C. for 4 hours. This was proved by mixed melt determinations.

Here was more evidence for the deactivating effect of nitro group or groups.

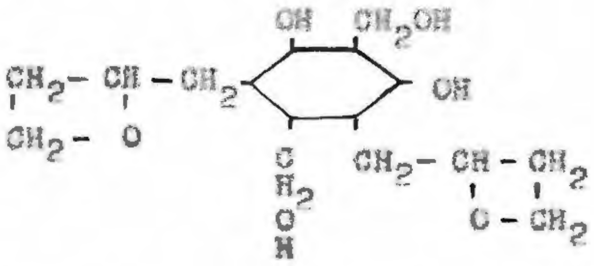
IV. 4-6 DIALLYLRESORCINOL.

The synthesis of this compound was a classical example of the Claisen Rearrangement. Firstly the diallyl ether of resorcinol was synthesised which on pyrolysis rearranged to 4-6 diallyl resorcinol. The diallyl ether of resorcinol was prepared by using the method attributed to Hurd, Greengard and Pilgrim (81) in which a mixture of resorcinol and potassium carbonate was reacted with allyl bromide in acetone. Owing to the shortage of allyl bromide the compound was synthesised bythe action of hydrobromic acid on allyl alcohol (61).

The conversion of the diallyl ether was carried out by a modification of the method of Hurd and co-workers (81).

On condensation with 40% formalin in the presence of an alkaline catalyst, the product obtained was a mixture and was separated into its two components by boiling it up in benzene and filtering it hot. The solid component was insoluble while the liquid readily dissolved. The benzene filtrate was allowed to stand until all the benzene had evaporated off and a brownish liquid resulted which was identified as the original compound 4-6 diallylresorcinol. The solid component was recrystallised from acetone and petroleum ether as a brown amorphous solid which did not melt but charred at 240°.

Prins (101, 102) made the first comprehensive study of the reaction of formaldehyde with ethylinic hydrocarbons and he claimed to have isolated a four membered cyclic ether ring from formaldehyde and styrene which indicated that one possible structure for the product might be



Under acidic conditions the condensation of 4-6 diallylresorcinol with 40% formalin yielded mainly the original product but also a very small quantity of a brownish amorphous material.

From the combustion results obtained it was impossible to ascribe a structure for the product which was assumed to be a resin.

V. 3-5 DIBROMO-β-RESORCYLIC ACID.

β-Resorcylic acid was prepared as before (71, 72) and was then brominated by dissolving the acid in glacial acetic acid and adding to it three moles of bromine in the same solvent (82, 83, 84, 85).

On condensing with 40% formalin under alkaline conditions a brown sludge was obtained which was recrystallised from alcohol and water.

A halogen estimation (loc. cit.) revealed the absence of halogen.

Once again the removal of bromine was clearly shown and from combustion results it would appear that the bromine was replaced by hydroxy groups. The possible structure for this compound was 2-3-4-5 tetrahydroxybenzoic acid. It had no melting point but charred at 260^{0}. In an aqueous and alcoholic solution it reacted with ferric chloride to give a light brown and black colouration respectively. It appeared that this was the first time that this compound had been isolated.

C. CHLOROMETHYLATION.

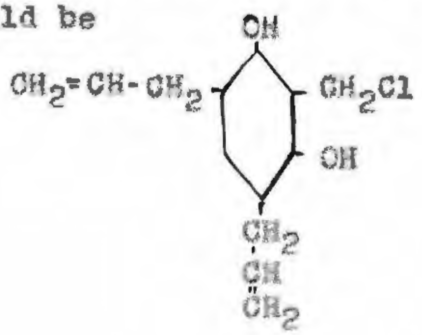
When it became apparent that the preparation of the primary condensation product by direct condensation of formalin under acidic and alkali conditions was very difficult to achieve and a new method of approach was adopted i.e. chloromethylation. The value of chloromethylation in the present work was in that the $-CH_2Cl$ group was convertable to the $-CH_2OH$ group.

The method employed was to saturate a solution of 40% formalin with hydrogen chloride gas, to this was added the compound and the resulting solution was well stirred and the hydrogen chloride was continually passed through. The reaction was allowed to run for two hours at 30°C. The reaction mixture was poured into ice and the solid material adhering to the apparatus was washed into a beaker with cold water. The impure compound was filtered off, washed thoroughly with cold water, dried and then purified.

I. 4-6 DIALLYLRESORCINOL.

The product was a brownish green solid which was purified by boiling up in benzene, then filtered to remove a small quantity of tar and on addition of petroleum ether to the benzene filtrate a pale brown amorphous substance was obtained which did not melt but charred at 250 °.

From analytical results it would appear that the compound had been chloromethylated and the possible structure would be



It was thought to be a mixture due to the low chlorine results but there was no possible means of separating it.

The attempted hydrolysis of this compound with silver oxide, however, failed.

No further work was possible on this topic because of supply difficulties.

II. GALLIC ACID.

Gallic acid was chloromethylated by the method previously described. The product obtained was pink and was recrystallised as long needles from alcohol or by dissolving in sodium hydroxide, neutralizing with acetic acid, followed by some sulphuric acid. The purified product did not melt but charred at 270° and gave a red colour with alkali.

From combustion results this compound was proved to be 2-2'-3-3'-4-4' hexa hydroxy-6-6' dicarboxyl diphenylmethane and was identical to the compound obtained by Möhlan and Kahl (86).

Condensation had taken place and in comparison with 5-nitro-β-resorcylic acid it appeared that the nitro group and not the carboxyl was responsible for the deactivation of the benzene nucleus.

III. 3-5 DIBROMO-β-RESORCYLIC ACID.

The chloromethylated product obtained here was a mixture of a white and brown material. The mixture was separated by treating the product with boiling water and filtering the hot solution. On cooling the filtrate, white needles separated which were identified as 3-5 dibromo-β-resorcylic acid by mixed melt determinations. There was only a very small quantity of brown material (± 1%) and the results were in support of Fuson and McKeever (87) who stated that the presence of halogen atoms on the ring caused the reaction to be more difficult to effect.

The brown compound was purified by continuous boiling with water. The product had no melting point but charred at 240°.

On analysis the results obtained were consistent with those of the compound 4-4'-6-6' tetrabromo-3-3'-5-5' tetrahydroxy-2-2' dicarboxyl diphenyl methane. This compound has not been described before. On treating an aqueous and alcoholic solution with ferric chloride, no colour was obtained in the former case but a greenish tinge in the latter.

Condensation has taken place and it would appear that the nitro and not the carboxyl group was responsible for the deactivating effect of the nucleus.

D. ATTEMPTED REDUCTION OF AN ALDEHYDE.

I. 3-5 DIBROMO-β-RESORCYLALDEHYDE.

3-5 Dibromo-β-resorcylaldehyde was synthesised by the bromination of β-resorcylaldehyde and the method of bromination employed constituted a new method of preparation of 3-5 dibromo-β-resorcylaldehyde.

The synthesis of β-resorcylaldehyde was performed by means of the Gattermann reaction on resorcinol. (61, 88). The bromination of β-resorcylaldehyde was performed by treating 1 mol of aldehyde with 3 mols of bromine. The brominating solvent was glacial acetic acid. The structure of the brominated product was confirmed by analysis and had a melting point of 200-201°.

Various methods of reduction were employed and the following methods were found to be of no use. (i) Aluminium ethylate, (ii) magnesium chloroethylate and (iii) glacial acetic acid and iron. The method which was successful was the catalytic hydrogenation of aldehydes using platinum oxide as catalyst (93).

The catalytic hydrogenation of 3-5 dibromo-β-resorcylaldehyde yielded a red gum which was found to be a mixture. It was separated into its components by dissolving in ether and an insoluble red tar was filtered off. On treating the ethereal solution with petroleum ether an orange amorphous compound was precipitated.

From the analysis it was impossible to ascribe any possible structure and it was thought to be a resin. The red tar was purified by treating with acetone and petroleum ether and its combustion results were almost identical to those of the orange amorphous product. Hence it appeared that the orange amorphous substance was identical to the red tar. However, the orange product was recrystallised again and more red tar was obtained. On being combusted again the results obtained were almost the same as before.

Hence it appeared that the substance obtained on the reduction of 3-5 dibromo-β-resorcylaldehyde was a resin. Carothers (93) reduced β-resorcylaldehyde to obtain a gum.

It was a known fact that phenolic alcohols were very sensitive to the action of minute traces of acid and since traces of acid were introduced with the ferrous chloride, the addition of alkali might be desirable as an aid in the isolation of the required alcohol. (13, 35, 93). The reduction was repeated and before filtering off the platinum some sodium hydroxide was added (93). On filtering off the platinum a clear solution was obtained but in a matter of seconds the solution darkened to a brownish orange colour. It appeared that a very unstable product was present which readily reacted to give a coloured product. The solvent was removed by vacuum distillation and a red gum was obtained. The product dissolved in ether but no red tar was obtained as in the last case. The ethereal solution was treated with petroleum ether and an orange amorphous substance was obtained. From analyses data, the product appeared to resemble that obtained in the last reduction.

Both orange amorphous compounds charred at 250°C., the acetyl derivative of each charred at between 195-200°C. and on treatment of an aqueous and alcoholic solution with ferric chloride no colouration was obtained by the former but in the case of the latter the solution darkened.

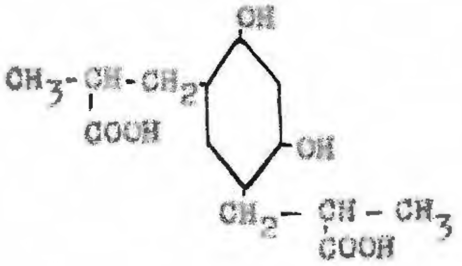
The reduction products resembled one another and no possible structural formula could be formulated. Hence the product was a resinous material.

II. 2-6 DIHYDROXY-3-5 DIALLYL BENZALDEHYDE.

The attempted synthesis of 2-6 dihydroxy 3-5 diallyl benzaldehyde by means of the Gattermann reaction on 4-6 diallyl resorcinol was a new synthesis and likewise the compound has not been described before.

The product was a black viscous liquid which was separated into a solid and liquid component by treating with ether, the former being insoluble in ether.

The solid component was recrystallised from chloroform and petroleum ether as a purple coloured material which sublimed at 185°C. The compound contained no nitrogen and did not give a precipitate with 2-4 dinitrophenylhydrazine. Hence it was neither an aldehyde nor a cyanide. To an alcoholic solution of the purple product some hydrochloric acid and sodium hydroxide were added respectively. The former solution remained purple but the latter changed to an orangish colour. On addition of hydrochloric acid to the alkaline solution, the purple colour was regenerated. Hence there was some evidence for the formation of a salt. It was thought that hydrogen cyanide had added across the double bond and the -CN group was hydrolysed to a carboxyl group. A possible structure for the acid was found to be and has not been described before.



The ether soluble component was obtained by distilling off the ether. This product gave a 2-4 dinitrophenylhydrazone which melted at 148°. The aldehyde was present in this mass. Actual purification could not be brought about since vacuum distillation failed, the compound did not form the sodium bisulphite addition complex and on attempted hydrolysis of the 2-4 dinitrophenylhydrazone with concentrated hydrochloric acid, no reaction took place even after boiling under reflux for 12 hours. Since the aldehyde could not be isolated from this viscous mass it was decided to prepare the 2-4 dinitrophenyl hydrazone which was purified by dissolving in acetone and precipitated on addition of water and to combust it. Microcombustion results offered strong evidence for the presence of a mono aldehyde group and the product was thus thought to be 2-6 dihydroxy-3-5-diallylbenzaldehyde.

Some of this aldehyde mixture was subjected to catalytic reduction. The pressure immediately dropped two pounds indicating that a reaction was taking place. The resulting solution was a port wine colour and on removal of ethanol under reduced pressure a black viscous liquid remained. A portion of this liquid was taken and treated with 2-4 dinitrophenylhydrazine. A distinct precipitate was obtained indicating that the aldehyde had not been reduced. The melting point of the dinitrophenylhydrazone was 112^{o}. Hence a reaction had definitely taken place as indicated by the drop in pressure and the melting point of the dinitrophenylhydrazone.

Shishkov (25) proved that in all cases the presence of another group between the hydroxy groups increased the chemical stability. Since the aldehyde was not reduced then the only possible reaction which could take place was the addition of hydrogen across the double bonds. Thus there was some 2-6 dihydroxy-3-5 dipropylbenzaldehyde in the viscous mass and could not be isolated.

Hence it was possible to come to the conclusion that some 2-6 dihydroxy-3-5 diallylbenzaldehyde was prepared by the Gattermann reaction on 4-6 diallyl resorcinol.

In April 1951 Finn and Musty (94) used lithium aluminum hydride for the reduction of phenolic aldehydes to phenolic alcohols but this method of reduction could not be employed because of the time it would take in obtaining the reagent.

The unfortunate shortages of allyl compounds prevented the full exploration of diallyl resorcinol. It would appear that a new line of attack would be the reduction of diallyl resorcinol to dipropyl resorcinol which would eliminate side effects due to the allyl double bond. Furthermore, dipropylresorcinol is a solid and hence would be much easier to work with.

4. CONCLUSIONS.

The present work has been performed in order to survey some possible lines of attack of the problem of the resorcinol-formaldehyde condensation. The direct condensation of blocked resorcinols with formaldehyde has failed. Evidently the phenolic alcohol if formed, was extremely reactive and condensed rapidly with any free positions in the ring of the neighbouring molecule. Furthermore, if a highly blocked molecule was used e.g. dibromo-β-resorcylic acid, dinitroresorcinol, 5 nitro-β-resorcylic acid the deactivating effects of the groups had to be considered and it was found that the nitro group was the main deactivating group and also steric effects appeared to arise.

The possibility of chloromethylation was demonstrated in the case of 4-6 diallyl resorcinol but supply difficulties prevented a thorough investigation. While the other compounds yielded methylene bis-derivatives.

A more reliable method would appear to be the reduction of an aldehyde to the alcohol. Evidently the reducing agents used were not satisfactory. Possibly lithium aluminum hydride which has very recently become generally available might be more successful as the reaction conditions were very mild. Ester reduction might also be used with advantage.

The experiments with saligenin have demonstrated that the condensation capacity of resorcinol depended on interaction of resorcinol with a resorcinyl alcohol and it was the activity of the latter rather than the former that was expedient.

5. EXPERIMENTAL.

A. CONDENSATION OF SALIGENIN WITH RESORCINOL.

1. SYNTHESIS OF SALIGENIN.

Saligenin was prepared by the catalytic reduction of salicylaldehyde. (93).

2. CONDENSATION OF SALIGENIN WITH RESORCINOL.

(a) ACID CATALYSED CONDENSATION AT ROOM TEMPERATURE.

1.24 gms of saligenin and 1.1 gms of resorcinol were condensed in 20 ml. 6 N sulphuric acid and in about five minutes a thickish white precipitate was obtained. The mixture was left to stand for an hour and the precipitate filtered off.

The compound was found to be soluble in ethanol, methanol, acetone, ether and isopropanol and in hot glacial acetic acid and water which on cooling yielded a milky suspension, insoluble in benzene, chloroform and petroleum ether. The best method of recrystallisation was from ether and petroleum ether. The compound darkened on standing and had a melting point of 180°C.

MICROCOMBUSTION OF COMPOUND

(1) 6.708 mg. of compound gave 3.465 mg. of H_2O and 17.661 mg. of CO_2

$$\%C = 71.80\%, \quad \%H = 5.78\%$$

(2) 6.934 mg. of compound gave 3.657 mg. H_2O and 18.487 mg. of CO_2

$\%C = 72.73\%, \quad \%H = 5.900\%$

(3) 5.937 mg. of compound gave 3.057 mg. H_2O and 15.606 mg. of CO_2

$\%C = 71.69\%, \quad \%H = 5.76\%$

Mean $\%C = 72.07\%, \quad \%H = 5.81\%$

$C_{13}H_{12}O_3$ required 72.21 %C, 5.55 %H

(b) ALKALI CATALYSED CONDENSATIONS.

(1) AT ROOM TEMPERATURE.

1.24 gms of saligenin and 1.1 gms of resorcinol were condensed in 100 ml. of 4% sodium hydroxide and the mixture was left to stand for a week. The mixture was neutralised with glacial acetic acid and extracted with ether. The ether was removed by distillation and a reddish coloured liquid was obtained which crystallised on cooling. The product was recrystallised from benzene and on examination of the crystals, needles and plates were observed. The former was characteristic of resorcinol and the latter of saligenin. On treating the product with benzene it all dissolved indicating the absence of 2-2'-4' trihydroxy diphenylmethane.

The separation of the saligenin-resorcinol mixture was very difficult but fractional crystallisation with benzene was employed. However, it gave good results for resorcinol but to remove the last traces of resorcinol from the saligenin was extremely difficult. The first fraction obtained consisted of resorcinol, melting point 110° and the yield was about a gram. but the other fractions had diffuse melting points varying from 70-83° which were low for the melting point of saligenin, 87°C and it seemed almost impossible to remove the last traces of resorcinol. In order to provide evidence for the above a mixture of resorcinol and saligenin was fractionally crystallised. The first fraction consisted of resorcinol while the other fractions had the same variation in melting points as was obtained before. Even after the fifth fraction a positive resorcinol test was observed by treating an aqueous solution with sodium hydroxide and one drop of chloroform, on heating a red colour was obtained.

Reaction between resorcinol and saligenin had not taken place.

(ii) At 60°C.

1.24 gms saligenin and 1.1 gms of resorcinol were condensed in 20 ml. of 6N sodium hydroxide at 60°C for 4 hours. On cooling, the solution solidified and the solid material was filtered off. The filtrate was neutralised with dilute acetic acid and extracted with ether. On distilling off the ether a solid was obtained which separated as needles from benzene. This product was identified as resorcinol by mixed melts. The yield was about a gram and once again it appeared that saligenin had not condensed with resorcinol. The solid material appeared to resemble saligenin. Some water and more alkali were added to it. The solid dissolved and the resulting solution was neutralised with dilute acetic acid. Then the neutral solution was extracted with ether, the ether distilled off and the product was recrystallised from benzene. The product melted at 88° and was identified as saligenin. Condensation between saligenin and resorcinol had failed.

(iii) AT 100°C.

The condensation was again repeated at 100°C for one hour with 0.4% sodium hydroxide solution. The solution was neutralised with dilute acetic acid and extracted with ether. On removal of ether a reddish liquid was obtained which crystallised on standing. The product appeared to resemble that obtained when condensation was carried out at room temperature and was suspected to be saligenin and resorcinol.

The same results were obtained as for (i) in the fractional crystallisation of the product and no insoluble product was observed. Reaction had failed.

(iv) SELF CONDENSATION OF SALIGENIN.

Some saligenin was heated at 100°C for an hour in a solution of 0.4% sodium hydroxide. The solution was neutralised with dilute acetic acid, extracted with ether,

ether removed, and the product was recrystallised from benzene. The product melted at 88°C and was identified as saligenin.

Saligenin will not condense with itself at 100°C.

B. REACTIONS BETWEEN FORMALDEHYDE AND SUBSTITUTED RESORCINOLS.

I. 4-6 DIBROMORESORCINOL

This compound was synthesised more successfully by Zehenter's method (60) than by Kohn and Löff's (62).

(1) PREPARATION OF 4-6 DIBROMORESORCINOL.

Zehenter's method consisted in adding two moles of cooled bromine in carbon disulphide to a cooled suspension of 1 mol resorcinol in the same solvent. Practically all the resorcinol dissolved and the liquid was quickly filtered becoming a solid crystalline mass on standing for a short time. The 4-6 dibromoresorcinol was purified by recrystallisation from water.

MODIFICATION.

It was found that the same yield could be obtained by not filtering and allowing the substance to crystallise out in the reaction flask. This modification was employed.

Kohn and Löff's method used carbon tetrachloride as the brominating solvent.

(2) CONDENSATION OF 4-6 DIBROMORESORCINOL WITH EXCESS FORMALIN.

(a) CONDENSATION AT ELEVATED TEMPERATURES.

(i) About 1 gm of 4-6 dibromoresorcinol was taken and dissolved in the minimum quantity of absolute alcohol.

To this solution was added 1 ml of 6 N hydrochloric acid followed by an excess of 40% formalin. The resulting solution was heated on a waterbath for about three hours at 60°C. and then evaporated to half volume.

At the commencement of the experiment the solution was colourless but on heating the colour changed to yellow and darkened with the formation of a brownish red precipitate.

The precipitate was filtered off and the filtrate was extracted with ether from which no solid material was obtained.

The experiment was repeated using (ii) acetic acid as solvent, (iii) by dissolving the dibromoresorcinol directly in formalin and using hydrochloric acid as the catalyst.

No obvious difference in the product for these three experiments was detected.

The condensed product was insoluble in methanol, acetic anhydride, glacial acetic acid, ether, acetone, chloroform, benzene, carbon disulphide, absolute ethanol, cyclohexanone, water but sparingly soluble in benzaldehyde to give a deep red solution. The product was very insoluble and on closer examination it was found to be amorphous.

An attempt to determine its molecular weight by the Rast Camphor Method (61) also failed because of the insolubility of the condensed product.

The condensed product had the following characteristics. (1) It was very insoluble. (2) It did not melt. (3) It was amorphous. It appeared to be a resin which was defined (63) as a solid or semi solid, complex, amorphous mixture of organic substances having no definite melting point and showing no tendency to crystallise.

(b) CONDENSATION AT ROOM TEMPERATURE.

(1) HYDROCHLORIC ACID CATALYSED.

About 1 gram of 4-6 dibromoresorcinol was treated with an excess of formalin (40%) and 1 ml of 6 N hydrochloric acid. The solution was left to stand for a week. At first the solution was colourless but acquired a faint yellow colour. A fine precipitate in exceedingly small quantities separated after the third day but the yield was so small that the precipitate was unworkable. The excess formalin was removed by very careful evaporation to about half the volume and the precipitate obtained was filtered off. The filtrate was extracted with ether from which no solid material was obtained. The precipitate when dry was a brown amorphous powder.

The product was insoluble in methanol, petroleum ether, ligroin, glacial acetic acid, ether, chloroform, water, benzene, xylene, sparingly soluble in hot acetone and soluble in hot n-butanol from which it was recrystallised.

The pure compound was brownish in colour, amorphous and had no melting point.

MICROCOMBUSTION OF PRODUCT

(1) 4.579 mg of compound gave 1.760 mg of H_2O and 5.955 mg of CO_2

$\%C = 35.46\%, \quad \%H = 4.3\%$

(2) 9.930 mg of compound gave 3.810 mg H_2O and 12.92 mg of CO_2

$\%C = 35.40\%, \quad \%H = 4.29\%$

Mean $\%C = 35.43\%, \quad \%H = 4.30\%$.

HALOGEN ESTIMATION

The Pringsheim Sodium Peroxide Fusion Method (64, 65, 66, 67) was employed.

(1) .1276 gms of product gave .1159 gm AgBr
$\%\ Br = 38.66\%$

(2) .1476 gm of product gave .1339 gms AgBr
$\%\ Br = 38.61\%$

Mean $\%\ Br = 38.64\%$.

To assign a structural formula having these given percentages was very difficult indeed.

This condensed product has all the characteristics of a resin i.e. very insoluble, no melting point and amorphous.

(2) ALKALI CATALISED.

1.3 gms of 4-6 dibromoresorcinol were dissolved in 100 ml of 1% sodium hydroxide and 0.4 gms of 40% formalin added. The resulting solution was left to stand for a week or better until the odour of formaldehyde disappeared.

The solution darkened on standing to a reddish brown colour by the end of the first day, but by the end of the week, it was black. The solution was acidified with glacial acetic acid. This was divided into two main portions. One of the portions was allowed to stand for a few days and a brown sludge was obtained while the other on treatment with ether immediately yielded a brown sludge. In both cases the supernatent liquid was removed by centrifuging.

The product was insoluble in water, benzene, absolute ethanol, methanol, acetone, glacial acetic acid, n-butanol, petroleum ether, xylene, ether and chloroform. The product was very insoluble and was purified by dissolving in sodium Hydroxide acidifying with glacial acetic acid and then adding ether.

The pure compound was brown in colour, amorphous and had no melting point.

MICROCOMBUSTION

(1) 5.611 mg of compound gave 3.243 mg H_2O and 10.01 mg of CO_2

%C = 48.64%, %H = 6.47%

(2) 5.152 mg of compound gave 2.956 mg H_2O and 9.091 mg of CO_2

%C = 48.11%, %H = 6.42%

Mean %C = 48.38%, %H = 6.44%

HALOGEN ESTIMATION

Only a minute trace of halide was found to be present. This compound appeared to be a resin.

(c) THE INVESTIGATION OF THE REMOVAL OF BROMINE FROM 4-6 DIBROMORESORCINOL.

Two specimens of 4-6 dibromoresorcinol were treated with some sodium hydroxide and 40% formalin respectively. The solutions were left to stand for a week.

(i) REACTION WITH 40% FORMALIN.

The solution was colourless and a precipitate was obtained on addition of 6 N nitric acid. The precipitate was filtered off and a positive halogen test was obtained on treating the filtrate with silver nitrate.

The formalin was responsible for the removal of some of the bromine.

(ii)α) REACTION WITH SODIUM HYDROXIDE.

The solution was yellow in colour and on acidifying with 6 N nitric acid a brownish precipitate was obtained which was filtered off. The filtrate yielded a positive test with silver nitrate.

The sodium hydroxide was responsible for removal of some of the bromine and was more efficient than the formalin.

β) SYNTHESIS OF 1:2:4:5 TETRAHYDROXYBENZENE.

About 2 grams of 4-6 dibromoresorcinol were treated with 100 ml of 6 N sodium hydroxide and the solution was heated for three hours on a waterbath. At the start the solution was colourless but darkened on heating to brown. Dilute sulphuric acid was added and colourless needles separated. This compound was recrystallised by dissolving in 6 N sodium hydroxide and the solution was just acidified with concentrated hydrochloric acid. The precipitate was filtered off and washed thoroughly with water. A halogen estimation was performed on the compound to find out if the bromines had been removed.

HALOGEN ESTIMATION

(1) .0691 gms of compound gave .0888 gm AgBr

%Br = 54.76%

(2) .0625 gms of compound gave .0865 gm AgBr

%Br = 58.89%

Mean %Br = 56.83%

This solid was the original compound and from the literature, it would appear that this compound was very sluggish in being precipitated from acid solution. Thus the derivative might be in solution.

Some more 4-6 dibromoresorcinol was boiled with 70% alkali for about an hour and the solution was acidified with concentrated hydrochloric acid but this time there was a small yield of a blackish substance. The solution was left exposed to the air for a few days. The crystals were examined under a microscope and were found to be small black, slender plates terminated by a single plane at an oblique angle and showing a yellow reflex and appeared to be identical to those obtained by Jackson and Beggs. (69) The presence of some tetrahydroxybenzene was indicated. Some of the alkali solution was kept, neutralised and treated with ferric chloride. A black precipitate was obtained and this result was in agreement with Nietzki and Schmidt (70). Thus there was more evidence as to the presence of some 1:2:4:5 tetrahydroxybenzene.

II. 5-NITRO-β-RESORCYLIC ACID.

This compound was synthesised by the nitration of β-resorcylic acid.

(1) SYNTHESIS OF β-RESORCYLIC ACID.

The required acid was prepared by the action of potassium bicarbonate and carbon dioxide on resorcinol in aqueous solution and the potassium salt of the acid was hydrolysed with concentrated hydrochloric acid to give β-resorcylic acid (71, 72).

(2) NITRATION OF β-RESORCYLIC ACID.

Various methods of nitration were employed and the best method was found to be that of "mixed acids" in which a yield of 60% was obtained.

METHOD (1) Parekh and Shah (73) obtained a yield of 55% by treating dry β-resorcylic acid with concentrated nitric acid and special precautions were taken against the water of the atmosphere. On repeating this work a yield of 45% was obtained and it was observed that on addition of concentrated nitric acid a very vigorous reaction occurred. It was also found that the nitrated product could not be recrystallised from methanol as was stated by Parekh and Shah but could from water and water-methanol mixture. The former gave long white needles, while the latter small needles.

Hemmelmayr (74) prepared styphnic acid and 5 nitro-β-resorcylic acid by nitrating resorcylic acid and in order to increase the yield of 5-nitro-β-resorcylic acid the reaction flask was placed in a freezing mixture (75, 76). The styphnic acid was removed by dissolving in water (76).

MODIFICATION. The Parekh and Shah method was repeated but the reaction flask was placed in a freezing mixture and the nitric acid was cooled before addition. Excess water was added to remove any styphnic acid and the yield of the 5-nitro-β-resorcylic acid was increased to 50%.

METHOD (ii) "Sodium nitrate and concentrated sulphuric acid".

5 grams of β-resorcylic acid were mixed with 5 ml concentrated sulphuric acid and the resulting mixture was placed in a freezing mixture. Then 5.2 gms of sodium nitrate were slowly added and the mixture vigorously stirred. The nitrating mixture was left to stand for 12 hours; diluted with a large excess of water and the nitrated acid filtered off. The yield of pure 5-nitro-β-resorcylic acid was about 40%.

METHOD (iii) Excess concentrated nitric acid.

The modified Parekh and Shah method was repeated but 36 ml of concentrated nitric acid were added to 5 gms of β-resorcylic acid. The yield was about 50%.

METHOD (iv) Mixed acids - concentrated nitric and sulphuric acids were employed.

30 ml of a mixture of 2:1 60% nitric acid and 99% sulphuric acid were thoroughly cooled and were added slowly and with constant stirring to 5 grams of β-resorcylic acid, contained in a round bottomed flask which was placed in a freezing mixture. The flask was left in the melting ice solution and then in the resulting ice water for 4 hours. When the ice water had attained the temperature of the room it was removed and the nitrating mixture was left to stand for 24 hours. Then a large quantity of water was added, the mixture well shaken and then filtered. The product was recrystallised from water and the yield was about 60%.

For the nitration of β-resorcylic acid to form 5-nitro-β-resorcylic acid the mixed acids method was employed.

5-nitro-β-resorcylic acid crystallised as yellow-straw coloured needles from either water or from a water-methanol mixture and had a melting point of 215°C.

(3) CONDENSATION OF 5-NITRO-β-RESORCYLIC ACID WITH 40% FORMALIN.

(a) ALKALINE CONDITIONS.

(i) One gram of sample was dissolved in about 2 ml of 6 N sodium hydroxide and (a) large excess of formalin (40%), (b) slight excess formalin, the solution being just acid, was added. After standing at room temperature for a week only the unchanged acid could be isolated. Thus no obvious reaction had occurred.

(ii) One gram of sample was dissolved in methanol, 1 ml of 6 N sodium hydroxide was added followed by (a) a large excess of formalin (40%) and (b) a slight excess. The solutions were left to stand for a week at room temperature and were both yellow in colour. Onlythe the unchanged acid could be isolated.

In both the above cases the products obtained were recrystallised from water and from mixed melting point data, it was deduced that no reaction had occurred.

The experiments were repeated by heating on a waterbath for 5 hours and once again reaction failed to take place.

(b) <u>ACIDIC CONDENSATIONS</u>.

The method employed here was that used by Fishmann (77) to obtain methylol derivatives of o-nitro-phenol.

1 gram of sample was condensed with (a) 0.5 gms and (b) 2.5 gms of 40% formalin in the presence of 3 grams concentrated hydrochloric acid. The mixture was allowed to stand at room temperature for a week and the material filtered off. This material was identified as 5-nitro-β-resorcylic by performing mixed melts.

The experiments were repeated by digesting on a sand bath at 60°C. for 4 hours and once again only the unchanged acid was isolated. This was proved by taking mixed melts.

III. 2-4 DINITRORESORCINOL.

2-4 Dinitroresorcinol was prepared by means of a two stage synthesis; (1) the synthesis of 2-4 dinitrosoresorcinol and (2) the oxidation of 2-4 dinitrosoresorcinol to the dinitro derivative.

(1) SYNTHESIS OF 2-4 DINITROSORESORCINOL.

This compound may be synthesised by either the Fitz's or Schultz's method (78). The former was found to give the better yield (±80%).

Briefly Fitz's method was to treat a cooled (0°C.) aqueous solution of resorcinol with glacial acetic acid; then an aqueous solution of 2 moles potassium nitrite was added. After a quarter of an hour, 2 moles of cooled dilute sulphuric acid were added. The mixture was then removed from the freezing mixture and allowed to stand for 1 hour. The crude precipitate of 2-4 dinitrosoresorcinol was filtered off and could be purified from 50% alcohol.

(2) OXIDATION OF 2-4 DINITROSORESORCINOL.

Kostanecki and Feinstein (79) oxidised 2-4 dinitrosoresorcinol to the required derivative by using concentrated nitric acid in the ratio of 1:4. The reaction was carried out in a freezing mixture in order to prevent the formation of styphnic acid which was removed by shaking up with a large quantity of water. The product was recrystallised from water and the yield was about 80%.

2-4 Dinitroresorcinol crystallised as flakes from water and had a melting point of 140°. The compound was sparingly soluble in methanol and acetone and soluble in chloroform.

(3) CONDENSATION OF 2-4 DINITRORESORCINOL WITH 40% FORMALIN.

(a) ALKALINE CONDENSATION

One gram of substance was dissolved in acetone; a small quantity of sodium hydroxide was added followed by (a) a large excess of 40% formalin and (b) a slight excess of 40% formalin. The solutions were left to stand for a week at room temperature. From the product only 2-4 dinitroresorcinol could be isolated and this was proved by mixed melts.

The procedure was carried out at 60°C. but again no reaction took place.

(b) ACIDIC CONDENSATION.

One gram of dinitro derivative was condensed with (a) 0.5 gms of 40% formalin and (b) 2.5 gms of 40% formalin, using 3.0 gms of concentrated hydrochloric acid as catalyst. The mixture was allowed to stand for a week at room temperature. After the given time the solid material was filtered off. It was identified as dinitroresorcinol, mixed with a small quantity of paraformaldehyde.

The condensations were repeated at 60°C. for 4 hours. In both cases a white and yellow solid were obtained. The former was proved to be paraformaldehyde. The yellow solid was recrystallised from water and was identified as unreacted dinitroresorcinol by mixed melting point determinations.

IV. 4-6 DIALLYLRESORCINOL.

4-6 Diallylresorcinol was prepared by first preparing the diallyl ether of resorcinol subjecting it to pyrolysis, when the required compound was obtained.

(1) SYNTHESIS OF DIALLYL ETHER OF RESORCINOL.

The method employed was that due to Hurd, Greengard and Pilgrim (81) who treated resorcinol in an acetone solution with anhydrous potassium carbonate and allyl bromide. Owing to the shortage of allyl bromide it was prepared by the action of hydrobromic acid on allyl alcohol (61). The yield of the diallyl ether was 60% in comparison with 83% as stated by Hurd and co-workers. Diallyl ether had the following characteristics, boiling point 135-140°C. at 3 mm, 160-168°C. at 22 mm, 150°C. at 4 mm and gave no colour change with ferric chloride.

(2) SYNTHESIS OF 4-6 DIALLYLRESORCINOL.

Hurd and co-workers (81) found that, in general, it was only necessary to heat the allyl ether to 175° - 210°C. for rearrangement to occur. The reaction completed itself in a very short time and was decidedly exothermic.

Furthermore, the original sharp allyl ether odour was replaced by a phenol like odour and purification was by vacuum distillation. Pyrolysis was found to be difficult due to the formation of a red tar and a number of modified methods for pyrolysis were employed.

(i) Heated to 210° - Hurd and co-workers method.

20 grams of the purified diallyl ether were placed in a flask which was heated on a sand bath to 210°C. When the diallyl ether was at a temperature in the region of 210°C. a very vigorous reaction occurred and the temperature rose to over 300°. A red tar was obtained which was soluble in acetone and formed a red solution in alkali solution. The reaction was highly exothermic and another method was used to prevent the formation of the red tar.

(ii) Reflux under Reduced Pressure.

5 grams of the ether were taken and refluxed under reduced pressure for 2½ hours and the product was distilled over at a given pressure. A very small quantity of tar was obtained and was observed on the bottom of the distilling flask.

(iii) Heating and then Reducing Pressure.

5 grams of ether were heated to about 195° and just as fumes appeared the pressure was reduced. This procedure was repeated for about 30 minutes. A very small quantity of tar was obtained after distillation.

Method (iii) was used because of the short time taken for the rearrangement to be completed and the yield was in the region of 55%. It was also found that quantities of less than 15 gms should be used in order to prevent the formation of a thick red tar which was in agreement with Hurd and co-workers.

Characteristics of 4-6 diallylresorcinol were boiling points 180-185°C. at 14 mm and 158-162°C. at 4mm. The freshly distilled solution was pale yellow in colour and darkened on standing. The colour changes given with ferric chloride in aqueous and alcoholic solutions were blue and dark green respectively.

(3) CONDENSATION OF 4-6 DIALLYLRESORCINOL WITH 40% FORMALIN.

(a) ALKALINE CONDENSATIONS.

The following solutions were prepared:-

(i) One gram of substance was dissolved in 100 ml of 1% sodium hydroxide and a large excess of 40% formalin was added. The solution was left to stand for 3 days.

(ii) One gram of substance was dissolved in 100 ml 1% sodium hydroxide and 1.0 gm of 40% formalin was added. The solution was left to stand for 3 days. This was the Manasse method which proved to be very successful in the preparations of methylol derivatives of phenol and its homologues.

Both solutions darkened on standing to a dark brown colour. At the end of the given time the solutions were treated with dilute acetic acid until just acidic and a light brown gum was obtained which was filtered off.

The gum was purified next. It was soluble in absolute alcohol, acetone, ethyl acetate, insoluble in petroleum ether, ether and water and it appeared to be sparingly soluble in hot benzene but on closer examination the insoluble product was a solid. The gum was a mixture and was separated as follows: The impure compound was heated in benzene and the hot solution was filtered. The benzene filtrate was allowed to stand until all the benzene had evaporated off and the product was then analysed. The benzene extract was a thick brown viscous liquid and the insoluble substance was a light brown solid which was also analysed.

MICROCOMBUSTIONS OF LIQUID

(1) 12.508 mg. of compound gave 8.268 mg. H_2O and 34.43 mg. of CO_2

%C = 75.08%, %H = 7.39%

(2) 8.871 mg. of compound gave 5.974 mg. H_2O and 24.49 mg. of CO_2

%C = 75.26%, %H = 7.53%

(3) 7.828 mg. of compound gave 5.303 mg. H_2O and 21.70 mg. of CO_2

%C = 75.60%, %H = 7.58%

Mean %C = 75.31%, %H = 7.50%

The liquid was the original compound 4-6 diallyl resorcinol (calculated %C = 75.78%, %H = 7.36%).

INSOLUBLE PRODUCT.

This compound was soluble in absolute alcohol, acetone, ethylacetate and insoluble in ether, petroleum ether, benzene and water. It was recrystallised from acetone and petroleum ether, and the pure compound was a brown amorphous solid which did not melt but charred at 240°.

MICROCOMBUSTIONS

(1) 6.945 mg. of compound gave 4.364 mg. H_2O and 15.882 mg. of CO_2

$\%C = 62.36\%, \quad \%H = 7.03\%$

(2) 8.316 mg. of compound gave 5.212 mg. H_2O and 19.135 mg. of CO_2

$\%C = 62.76\%, \quad \%H = 7.01\%$

(3) 7.312 mg. of compound gave 4.628 mg. H_2O and 16.666 mg. of CO_2

$\%C = 62.22\%, \quad \%H = 7.08\%$

Mean $\%C = 62.45\%, \quad \%H = 7.04\%$

$C_{16}H_{22}O_5$ required 62.22%C, 5.15%H

(b) ACIDIC CONDENSATION.

1 gm. of 4-6 diallylresorcinol was condensed with 1 ml. 40% formalin in the presence of 5 ml. (a) concentrated hydrochloric acid and (b) 1:1 sulphuric acid. Both mixtures were left to stand for a week at room temperature and (b) was boiled for five minutes

after standing for the given time at room temperature. In both cases a thick brown liquid was obtained which was separated from reaction mixture by decantation and was washed thoroughly with distilled water. Both products were dissolved in ether and it was observed, that in (a) there was a small quantity of insoluble material which was brownish in colour and this solid was filtered off. The yield was so small that it was purified by washing with hot water. This compound gave a negative paraformaldehyde test with resorcinol and concentrated sulphuric acid and was then subjected to combustion.

MICROCOMBUSTION OF SOLID.

2.784 mg. of compound gave 1.640 mg. H_2O and 6.026 mg. of CO_2

$\%C = 59.03\%$, $\%H = 6.59\%$

Compound appeared to be a resin.

MICROCOMBUSTION OF LIQUID OBTAINED FROM (a).

(1) 5.764 mg. of compound gave 3.771 mg. H_2O and 15.80 mg. CO_2

$\%C = 74.76\%$, $\%H = 7.32\%$

(2) 5.977 mg. of compound gave 4.020 mg. H_2O and 16.41 mg. CO_2

$\%C = 74.87\%$, $\%H = 7.52\%$

Mean $\%C = 74.82\%$, $\%H = 7.42\%$

MICROCOMBUSTION OF LIQUID OBTAINED FROM (b).

(1) 7.644 mg. of compound gave 5.151 mg. H_2O and 20.96 mg. CO_2

$\%C = 74.78\%, \quad \%H = 7.54\%$

(2) 6.718 mg. of compound gave 4.537 mg. H_2O and 18.45 mg. CO_2

$\%C = 74.91\%, \quad \%H = 7.55\%$

Mean $\%C = 74.85\%, \quad \%H = 7.55\%$

From the percentages obtained the brownish liquid appeared to be the original 4-6 diallylresorcinol.

V. 3-5 DIBROMO-β-RESORCYLIC ACID.

(1) SYNTHESIS OF 3-5 DIBROMO-β-RESORCYLIC ACID.

β-Resorcylic acid was prepared as before (71, 72) and was then brominated by dissolving the acid in glacial acetic acid and to it was added three moles of bromine in the same solvent (82, 83, 84, 85).

(2) CONDENSATION OF 3-5 DIBROMO-β-RESORCYLIC ACID WITH 40% FORMALIN.

The Manasse method was employed. A mixture of 2.8 gms of dibromo derivative, 0.75 gms of formalin and 100 ml. 1% sodium hydroxide was left to stand for a week during which time the solution darkened from brownish yellow to black. It was then treated with dilute hydrochloric acid until slightly acidic. A brown sludge was obtained. To the acidic solution in a separatory funnel some absolute alcohol was added in order to dissolve the sludge followed by some ether. The ether-alcohol extract was kept and distilled under reduced pressure to about an eighth of the volume. On addition of water a brown precipitate was obtained which appeared to be microscopic crystals.

The substance so obtained was found to be soluble in absolute alcohol, methanol, acetone, acetic acid and ethyl acetate, insoluble in water, benzene, petroleum ether and chloroform, and soluble in hot ether. The compound was purified by dissolving in alcohol and reprecipitated by addition of water.

(i) <u>HALOGEN ESTIMATION</u> indicated that the compound was halogen free.

(ii) <u>MICROCOMBUSTIONS</u>

(1) 7.098 mg. of compound gave 2.382 mg. H_2O and 11.18 mg. CO_2

%C = 42.94%, %H = 3.78%.

(2) 7.352 mg. of compound gave 2.452 mg. H_2O and 11.60 mg. CO_2

%C = 43.03%, %H = 3.73%.

Mean %C = 42.99%, %H = 3.75%

$C_7H_6O_6$ $\frac{1}{2}$ H_2O required %C = 43.03%,

%H = 3.59%

It was later shown that dibromo-resorcylic acid lost bromine when treated with alkali.

C. CHLOROMETHYLATION

I. 4-6 DIALLYL RESORCINOL.

A solution of 6 ml. 40% formalin in 8 ml. concentrated hydrochloric acid was saturated with gaseous hydrogen chloride. The temperature was raised to 30° and then 1.9 grams of 4-6 diallylresorcinol were added. The mixture was stirred vigorously for two hours while a brisk stream of hydrogen chloride was passed through it. The hydrogen chloride generator consisted of concentrated sulphuric acid in a large flat bottomed flask to which was attached a delivery tube and a separatory funnel with a long stem which enabled concentrated hydrochloric acid to flow into the concentrated sulphuric acid (61).

The allyl derivative did not dissolve and after about an hour a brownish green solid was deposited. The temperature was maintained at 30° for the required two hours. The reaction mixture was poured into ice and the solid material adhering to the apparatus was washed into the beaker with cold water. The solid mass was filtered off and washed with cold water.

The product was insoluble in petroleum ether, absolute alcohol, methanol, acetone and water, soluble in hot m-xylene, ethyl acetate ether, dioxane and trichloroethane (sym) but on treatment with hot benzene the bulk of the product was soluble except for a tarry residue. The impure product was purified by boiling with benzene and the resulting solution filtered in order to remove the tar. On addition of petroleum ether a pale brownish precipitate was obtained. Other mixed solvents such as ether and petroleum ether, dioxane and petroleum ether, and trichloroethane and petroleum ether yield a sticky gum.

(i) MICROCOMBUSTION OF COMPOUND.

(1) 6.207 mg. of compound gave 3.386 mg. H_2O and 14.914 mg. CO_2

%C = 65.51%, %H = 6.10%

(2) 7.759 mg. of compound gave 4.267 mg. H_2O and 18.62 mg. CO_2

%C = 65.45%, %H = 6.15%

Mean %C = 65.49%, %H = 6.13%

(ii) HALOGEN ESTIMATION

(1) .1692 gm. of compound gave .05856 gm. AgCl

%Cl = 8.561%

(2) .2211 gm. of compound gave .08698 gm. AgCl

%Cl = 9.729%

Mean %Cl = 9.145%

The fusions never worked properly even when a lot of sugar was added because specks of unchanged material were observed in solution.

$C_{13} H_{15} O_2$ Cl required %C = 65.40%, %H = 6.290%
%Cl = 14.88%

(2) TREATMENT OF CHLOROMETHYL DERIVATIVE OF 4-6 DIALLYLRESORCINOL WITH SILVER OXIDE.

1 gram of the product was added to 20 ml. absolute alcohol and 3 grams of silver oxide and left on a shaker for twelve hours. The resulting solution was filtered and filtrate was distilled under reduced pressure to see if any soluble product had been formed but that was not so. The silver oxide was removed from the solid by means of ammonia and the precipitate was washed with water. It was purified from benzene and petroleum ether, had no melting point and gave a greenish colour with ferric chloride. Hence hydrolysis had failed since the product possessed all the characteristics of the original compound.

II. GALLIC ACID.

Gallic acid was chloromethylated using the method previously described. The quantities of substance used were 17 grams of gallic acid, 60 ml. of 40% formalin and 80 ml. concentrated hydrochloric acid. The material turned pink in colour as the reaction proceeded.

The product was sparingly soluble in absolute alcohol, acetone, isopropanol and water and insoluble in ether, benzene and petroleum ether. The compound was recrystallised by dissolving in sodium hydroxide and a bright red colour was obtained; then 6 N acetic acid was added until the red colour disappeared followed by 1 ml. 6 N sulphuric acid. On standing needle shaped crystals were obtained. Some needles were treated with potassium cyanide and a magenta colour was not obtained which indicated that the needles were not gallic acid.

According to the work of Möhlau and Kahl (86) 2-2'-3-3'-4-4' hexahydroxy-6-6' dicarboxy diphenyl methane could be prepared by the action of hot concentrated hydrochloric acid and formaldehyde on a hot solution of gallic acid. The product was fairly soluble in water but dissolved more readily in dilute alcohol from which it recrystallised in long white needles. The pure product did not melt but charred and turned red in alkali solution.

A portion of the pure material was boiled up in a large quantity of alcohol, filtered and the filtrate yielded white needles on cooling. The product did not melt but charred at 270° and as has already been mentioned gave a red colour with alkali. The compound appeared to be identical with that obtained by Möhlau and Kahl.

MICROCOMBUSTIONS

(1) 7.296 mg. of compound gave 2.374 mg. H_2O and 13.78 mg. CO_2

$\%C = 51.51\%$, $\%H = 3.64\%$

(2) 7.074 mg. of compound gave 2.320 mg. H_2O and 13.35 mg. CO_2

$\%C = 51.47\%$, $\%H = 3.67\%$

Mean percentage 51.49%C, 3.65%H.

$C_{15}H_{12}O_6$ required 51.14%C, 3.41 %H.

III. 3-5 DIBROMO-β-RESORCYLIC ACID.

This compound was subjected to chloromethylation by the method already described and the quantities of substance taken were 5.6 gms of the bromo derivative, 15 gms of 40% formalin and 20 ml. of concentrated hydrochloric acid.

The product appeared to be a mixture of a whitish and brownish compound. The whitish compound was found to be soluble in hot water while the brown one was not. The mixture was separated by treating the product with boiling water and filtering the hot solution. On cooling the filtrate white needles separated.

The soluble portion was identified as unchanged 3-5 dibromo-β-resorcylic acid.

The brown solid was found to be insoluble in water, absolute alcohol, methanol benzene, chloroform and sparingly soluble in acetone and hot ether and was purified by prolonged boiling with water. The yield was 1%.

MICROCOMBUSTION OF COMPOUND

(1) 6.621 mg. of compound gave 0.895 mg. H_2O and 6.908 mg. CO_2

$\%C = 28.44\%, \quad \%H = 1.51\%$

(2) 6.602 mg. of compound gave 0.914 mg. H_2O and 6.807 mg. CO_2

%C = 28.12%, %H = 1.55%

Mean %C = 28.28%, %H = 1.53%

$C_{15}H_8O_8Br_4$ required 28.3% C, 1.258 %H.

D. REDUCTION OF AN ALDEHYDE.

I. 3-5 DIBROMO-β-RESORCYLALDEHYDE.

This compound was prepared by a two stage synthesis.

(1) Synthesis of β-Resorcylaldehyde.
(2) Bromination of β-Resorcylaldehyde.

(1) SYNTHESIS OF β-RESORCYLALDEHYDE.

The Gattermann reaction was employed for the preparation of the aldehyde. The aldehyde was prepared (61, 88) by mixing resorcinol in sodium dried ether with anhydrous zinc cyanide, the latter being prepared by the action of sodium cyanide on zinc chloride in alcoholic solution (61). A stream of dry hydrogen chloride was passed through the mixture liberating hydrogen cyanide (which reacted in situ) with the formation of the aldimine group. The ether was distilled off and the aldimine was hydrolysed with boiling water. The hot solution was filtered off and the β-resorcylaldehyde crystallised out.

(2) BROMINATION OF β-RESORCYLALDEHYDE.

This was a new method for the preparation of 3-5 dibromo-β-resorcylaldehyde.

To 1 mol of β-resorcylaldehyde in glacial acetic acid was added 3 moles of bromine also in glacial acetic acid and the solution was stirred vigorously.

A thick precipitate was obtained and filtered off.

Very little has been published about this compound and some research was done on it.

The compound was soluble in acetone, n-butanol, ether and hot absolute alcohol, methanol, chloroform, benzene and glacial acetic acid, insoluble in petroleum ether and sparingly soluble in hot water which on cooling yielded a crop of needle shaped crystals. Since a very large quantity of water was required for recrystallisation a mixture of 2 parts alcohol to 1 part water was preferred. The product, however, was slightly pink in colour.

(i) HALOGEN ESTIMATION

(1) 0.2652 gms. compound gave 0.3315 gms. of Aq Br

% Br = 53.2%

(2) 0.2409 gms. compound gave 0.3085 gms. of Aq Br

% Br = 54.51%

Mean % Br = 53.86%

(ii) MICROCOMBUSTIONS

(1) 9.185 mg. compound gave 1.623 mg. H_2O and 9.665 mg. CO_2

%C = 28.70%, %H = 1.98%

(2) 6.933 mg. compound gave 1.197 mg. H_2O and 7.319 mg. CO_2

%C = 28.78%, %H = 1.93%

Mean %C = 28.74%, %H = 1.96%

From the results there was no doubt that the compound was 3-5 dibromo-β-resorcylaldehyde. ($C_7H_4O_3Br_2$ required 28.38 %C, 1.352 %H, 54.05 %Br).

Henry and Sharp (90) found that the corrected melting point for 3-5 dibromo-β-resorcylaldehyde was 204° and in this case the uncorrected value was 200-201°.

A number of derivatives of 3-5 dibromo-β-resorcylaldehyde were prepared and their melting points recorded. Diacetate 114°, 2-4 dinitrophenylhydrazone 288° and then immediately decomposed.

Having obtained the dibromo derivative in such an excellent yield, it was next subjected to reduction in order to obtain the alcohol. Various methods of reduction were employed and results will be recorded.

(3) ATTEMPTED REDUCTION OF 3-5 DIBROMO-β-RESORCYLALDEHYDE.

(a) BY ALUMINUM ETHYLATE.

Aluminum ethylate was prepared by the action of aluminum powder on absolute alcohol in xylene (89). The reaction was catalysed by mercuric chloride and iodine.

(i) Reduction in the cold (89).

1.5 grams of 3-5 dibromo-β-resorcylaldehyde was dissolved in 10 ml. of absolute alcohol. To this solution was added 1 gram of aluminum ethylate and the mixture was allowed to stand for a week. No odour of ethyl acetate was observed during the standing period and it appeared that no reaction was taking place. After the allotted time most of the alcohol was removed by distillation and to the remaining solution some dilute sulphuric acid was added, until acidic. A precipitate was obtained but nevertheless, the acidified solution was extracted with ether. The ether was evaporated off and the product was recrystallised from water.

Melting point of compound = 199°C.

Mixed melt with 3-5 dibromo-β-resorcylaldehyde = 200°

The reduction had failed to take place.

(ii) Under reflux conditions.

A mixture of 1.5 gms. dibromo derivative, 10 ml. absolute alcohol and 1 gm. aluminum ethylate was refluxed for nine hours in a hydrogen atmosphere i.e. hydrogen was bubbled through the solution. The solution was filtered while hot, the bulk of the alcohol was evaporated off and the remaining solution was acidified with dilute sulphuric acid. The resulting acidic solution was extracted with ether. The product which was obtained after the distillation of ether was recrystallised from a water-alcohol mixture and melted at 200°. Mixed melt with 3-5 dibromo-β-resorcylaldehyde was 201°C. Reduction had again failed to take place.

(b) MAGNESIUM CHLOROETHYLATE (89).

The magnesium chloroethylate was not isolated in the pure state but was prepared in the reaction solution. A solution of 0.75 gms of dry hydrogen chloride in 19 ml. absolute ethanol was treated with 0.5 gms of magnesium filings. After the initial vigor of the reaction had subsided somewhat, the mixture was heated under reflux on a steam bath until all the magnesium had dissolved. To the resulting solution 1.5 gms of dibromo derivative, dissolved in 10 ml. absolute ethanol was added. The mixture was boiled under reflux conditions in an hydrogen atmosphere for about 11 hours. The bulk of the alcohol was removed by distillation and the resulting solution was acidified with dilute sulphuric acid. A precipitate was obtained and filtered off. On extracting the filtrate with ether, no solid material was obtained. The precipitate was recrystallised from water or ethanol-water mixture.

Melting point compound = 201°
Mixed melt with 3-5 dibromo-β-resorcylaldehyde = 201°

Reduction of 3-5 dibromo-β-resorcylaldehyde had failed to take place.

(c) GLACIAL ACETIC ACID AND IRON (91).

1.5 grams of dibromo derivative was refluxed with 10 grams of iron filings and 100 ml. of glacial acetic acid for 8 hours. At the end of this time the iron was filtered off and the bulk of the acetic acid removed by distillation. The solution was made alkaline and a gelatinous precipitate was obtained which was presumably iron hydroxide and filtered off. The filtrate was acidified with sulphuric acid and a white precipitate was obtained which was recrystallised from water.

Melting point of compound = 200°
Mixed melt with dibromo derivative = 201°

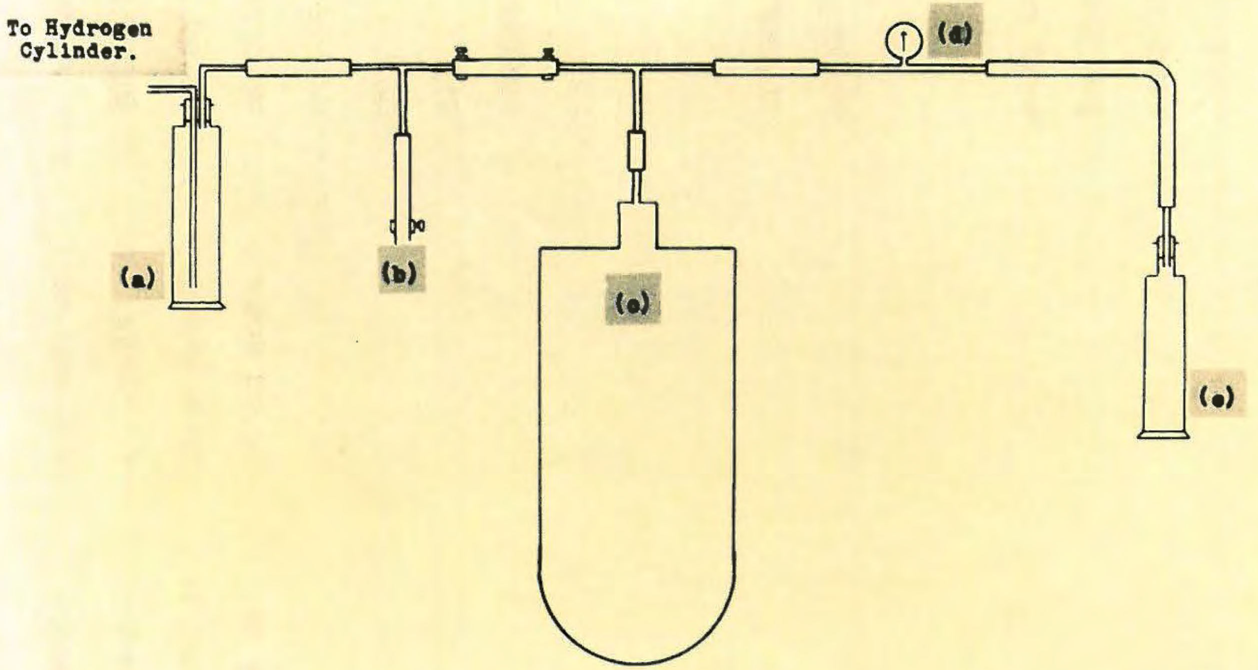
Therefore no reaction had taken place.

(d) THE CATALYTIC HYDROGENATION OF ALDEHYDES USING PLATINUM OXIDE AS CATALYST.

Preparation of Platinum Oxide.

The first step was to prepare ammonium chloroplatinate (91) by treating platinum or platinum residues with aqua regia and then to evaporate the solution to dryness a number of times with hydro-

CATALYTIC HYDROGENATION APPARATUS.



(a) Thick Walled Bottle Containing Charcoal and Soda-Lime, (b) Connected to Vacuum Pump, (c) Hydrogen Tank, (d) Pressure Gauge, (e) Thick Walled Reaction Flask.

chloric acid until free from nitrates. Then more hydrochloric acid was added, followed by an excess of ammonium chloride. The ammonium chloroplatinate was obtained and filtered off. A mixture of 3 grams of ammonium chloroplatinate and 30 gms of sodium nitrate, in a casserole (91, 92) was heated gently at first until the evolution of gas slackened, and then more strongly until a temperature of 500° was reached. This temperature was maintained for half an hour, cooled and the solid mass was dissolved in 50 ml. of water. The brown precipitate settled at the bottom, was washed well by decantation and filtered off using hardened filter paper. Then it was washed on the filter until practically free from nitrate. Thus the platinum oxide was prepared and was dried in a dessicator. The yield was 1.5 grams and was in agreement with Bruce's result (92). For complications due to improper fusion see Blatt and Gelman (91).

Purification of Hydrogen.

Before carrying out the reductions it was necessary to find out the impurities in the hydrogen in order to prevent the poisoning of the platinum oxide. A complete analysis was obtained from African Oxygen and Acetylene (Pty)., Ltd., and the impurities present were water and carbon dioxide to the extent of .0006 gm. per litre. The hydrogen was purified by passing it through a container containing charcoal and soda lime before it was allowed to enter the hydrogen tank.

Apparatus.

The apparatus used for the reduction of the aldehyde was set up as shown in diagram.

Procedure.

The procedure was that due to Carothers (93).

7.4 gms. of dibromo-β-resorcylaldehyde was dissolved in 150 ml. of 95% alcohol and to this solution was added 0.06 ml. of 0.2M ferrous chloride which acted as a promoter for the catalyst and 0.03 gms. of catalyst. The bottle containing the mixture was placed on the shaker, connected to the hydrogen tank and evacuated until the solvent boiled. Hydrogen was then admitted to a pressure of three atmospheres and immediately dropped a pound. Thus it appeared that the reduction was spontaneous but nevertheless the shaker was set in motion and left to run for 5½ hours to ensure that the reaction had taken place. During this time there was no decrease in pressure. The shaker was stopped, the hydrogen pumped out and air let in. The platinum oxide was filtered off with suction using very hard filter paper and an orange coloured solution was obtained. The solvent was removed by distillation under reduced pressure and a red gum was obtained.

The red gum wassoluble in absolute alcohol, methanol, acetone, n-butanol, ether and glacial acetic acid, insoluble in petroleum ether and water, sparingly soluble in benzene and chloroform. The product was finally recrystallised from ether and petroleum ether. On dissolving the compound in ether an insoluble red tar was obtained and filtered off, then the petroleum ether was added to the ethereal solution and an orange amorphous compound was obtained which did not melt.

(i) MICROCOMBUSTIONS OF ORANGE COLOURED COMPOUND.

(1) 7.247 mg. compound gave 1.690 mg. H_2O and 9.678 mg. of CO_2

%C = 36.42%, %H = 2.61%

(2) 7.493 mg. compound gave 1.760 mg. H_2O and 9.893 mg. of CO_2

%C = 35.99%, %H = 2.63%

Mean %C = 36.21%, %H = 2.62%

(ii) HALOGEN ESTIMATION OF ORANGE COMPOUND.

(1) .1867 gms. of compound gave .1911 gm. AqBr

% Br = 43.56%

(2) .1448 gms. of compound gave .1559 gm. AqBr

% Br = 45.81%

Mean % Br = 44.69%

These figures gave no indication as to a possible structure.

The red tar was recrystallised from acetone and petroleum ether.

(iii) MICROCOMBUSTION OF RED TAR.

(1) 6.993 mg. compound gave 2.055 mg. H_2O and 9.343 mg. of CO_2

%C = 36.42%, %H = 3.29%

(2) 6.200 mg. compound gave 1.624 mg. H_2O and 8.342 mg. CO_2

%C = 36.69%, %H = 2.93%

Mean %C = 36.56%, %H = 3.11%

The combustion results indicated that the red tar was identical with the orange amorphous product.

The orange amorphous product was recrystallised again and on dissolving in ether more red tar was obtained.

(iv) MICROCOMBUSTION OF RECRYSTALLISED ORANGE PRODUCT.

(1) 7.961 mg. compound gave 2.417 mg. H_2O and 10.784 mg. of CO_2

%C = 36.93%, %H = 3.39%

(2) 6.525 mg. compound gave 1.677 mg. H_2O and 8.892 mg. CO_2

%C = 37.17%, %H = 2.88%

Mean %C = 37.05%, %H = 3.14%

The reduction product was an amorphous resinous material.

It was a known fact that phenolic alcohols were very sensitive to the action of minute traces of acid and since traces of acid were introduced with the ferrous chloride, the addition of alkali might be desirable as an aid in the isolation of the required alcohol (13, 35, 93). The reduction was repeated with 0.2 ml. of N sodium hydroxide. (93)

On filtering off the platinum catalyst a crystal clear solution was obtained but in a matter of minutes the solution darkened to a brownish orange colour. Hence the presence of a very unstable compound was expected which would be very difficult to isolate due to its reactivity. The solvent was removed by vacuum distillation and a red gum was obtained. It resembled that obtained in the last reduction and was recrystallised from ether and petroleum ether. The purified product was an orange amorphous substance and did not melt.

(v) MICROCOMBUSTION OF ORANGE COMPOUND.

(1) 7.291 mg. compound gave 1.653 mg. H_2O and 9.669 mg. CO_2

%C = 36.16%, %H = 2.53%

(2) 7.751 mg. compound gave 1.816 mg. H_2O and 10.372 mg. CO_2

%C = 36.48%, %H = 2.62%

Mean %C = 36.32%, %H = 2.58%

This product was identical to that obtained in the last reduction.

II. 2-6 DIHYDROXY-3-5 DIALLYL-BENZALDEHYDE.

(1) SYNTHESIS OF 2-6 DIHYDROXY-3-5 DIALLYL BENZALDEHYDE BY THE GATTERMANN REACTION.

The aldehyde was prepared by mixing 10 gms of 4-6 diallyl resorcinol in 175 ml. of sodium dried ether, with 20 gms of anhydrous zinc cyanide in a three necked flask fitted with a mercury sealed stirrer, inlet tube for hydrogen chloride gas and outlet tube attached to an absorption system (61). A rapid stream of hydrogen chloride was passed through the mixture liberating hydrogen cyanide. The solution turned purple as the zinc cyanide dissolved and the product changed to black and separated as a thick oil. The experiment was run for 2½ hours and the ether distilled off. The product was refluxed for ¼ hour with dilute hydrochloric acid. After cooling the supernatent liquid was poured into a beaker of ice containing some hydrochloric acid and a thick blackish purple liquid remained in the flask. The supernatent liquid was left to stand in ice for 24 hours and a purplish liquid was obtained. Both purplish black liquids were dissolved in alcohol and transferred to the same container. The alcohol was distilled off under reduced pressure and a blackish purple liquid was obtained which had the smell of benzaldehyde. Purification of the blackish product by vacuum distillation proved to be unsuccessful.

The product was soluble in absolute alcohol, methanol, acetone, benzene, chloroform, glacial acetic acid, insoluble in water and petroleum ether. On being dissolved in ether, a solid product was observed. Hence the product was a mixture and was separated into a liquid and solid component by treating with ether.

SOLID COMPONENT.

This component was soluble in absolute alcohol, methanol, acetone, benzene, chloroform and glacial acetic acid, insoluble in water, petroleum ether and ether. It was recrystallised from chloroform and petroleum ether. Other mixed solvents such as acetone and petroleum ether, and benzene and petroleum ether yield a sludge.

The pure substance was purple in colour and sublimed at 185°C. The compound contained no nitrogen and did not give a precipitate with 2-4 dinitrophenylhydrazine. Hence it was neither an aldehyde nor a cyanide.

To an alcoholic solution of the purple product some 6 N hydrochloric acid and 6 N sodium hydroxide were added respectively. The former solution remained purple but the latter solution changed to an orangish colour. If some hydrochloric acid was added to the alkaline solution the purple colour was regenerated. Here there was some evidence for the formation of a salt.

MICROCOMUBSTION

(1) 7.901 mg. compound gave 4.187 mg. H_2O and 17.60 mg. CO_2

$\%C = 60.74\%, \quad \%H = 5.93\%.$

(2) 7.265 mg. compound gave 4.002 mg. H_2O and 15.998 mg. CO_2

$\%C = 60.06\%, \quad \%H = 6.16\%$

Mean $\%C = 60.40\%, \quad \%H = 6.04\%$

$C_{14}H_{18}O_6$ required 59.60%, %C, 6.38%, %H.

ETHER SOLUBLE COMPONENT

On evaporation of the ether a black viscous product was obtained. This product gave a 2-4 dinitrophenylhydrazone which melted at 148°. The aldehyde was present in this mass. Actually purification could not be brought about since vacuum distillation failed, the compound did not form the sodium bisulphite addition complex and on hydrolysis of the 2-4 dinitrophenylhydrazone with concentrated hydrochloric acid no reaction took place even after boiling under reflux for 12 hours. Since the aldehyde could not be isolated from this viscous mass it was decided to prepare the 2-4 dinitrophenylhydrazone which was purified from acetone and water and to combust it.

(1) MICROCOMBUSTION OF PHENYLHYDRAZONE.

(1) 7.039 mg. of compound gave 3.273 mg. H_2O and 14.014 mg. CO_2

%C = 54.26%, %H = 5.200%

(2) 6.190 mg. of compound gave 2.864 mg. H_2O and 12.364 mg. CO_2

%C = 54.45%, %H = 5.18%

(3) 6.254 mg. of compound gave 2.865 mg. H_2O and 12.468 mg. CO_2

%C = 54.37%, %H = 5.13%

Mean %C = 54.36%, %H = 5.17%

$C_{19}H_{18}O_6N_4 \cdot H_2O$ required 54.8 %C, 4.806 %H.

There was very strong evidence in favour of the presence of the aldehyde.

(2) CATALYTIC REDUCTION OF ALDEHYDE.

2.6 gms of aldehyde mixture, .015 gms of catalyst, 100 ml. 95% ethanol, .03 ml. 0.2M ferrous sulphate and .1 ml. N sodium hydroxide were placed in the reaction flask and the procedure was carried out identically as in the case of 3-5 dibromo-β-resorcylaldehyde. The pressure immediately dropped 2 lbs. at the start but remained the same throughout the shaking period. The resulting solution was a port wine colour and on removal of the ethanol under reduced pressure a black viscous liquid remained. A portion of this liquid was treated with

2-4 dinitrophenylhydrazine and a precipitate was obtained which indicated that the aldehyde group had not been reduced. The melting point of the 2-4 dinitrophenylhydrazone was 112° but darkened at 85°. From this it was concluded that the allyl groups had been hydrogenated to propyl groups.

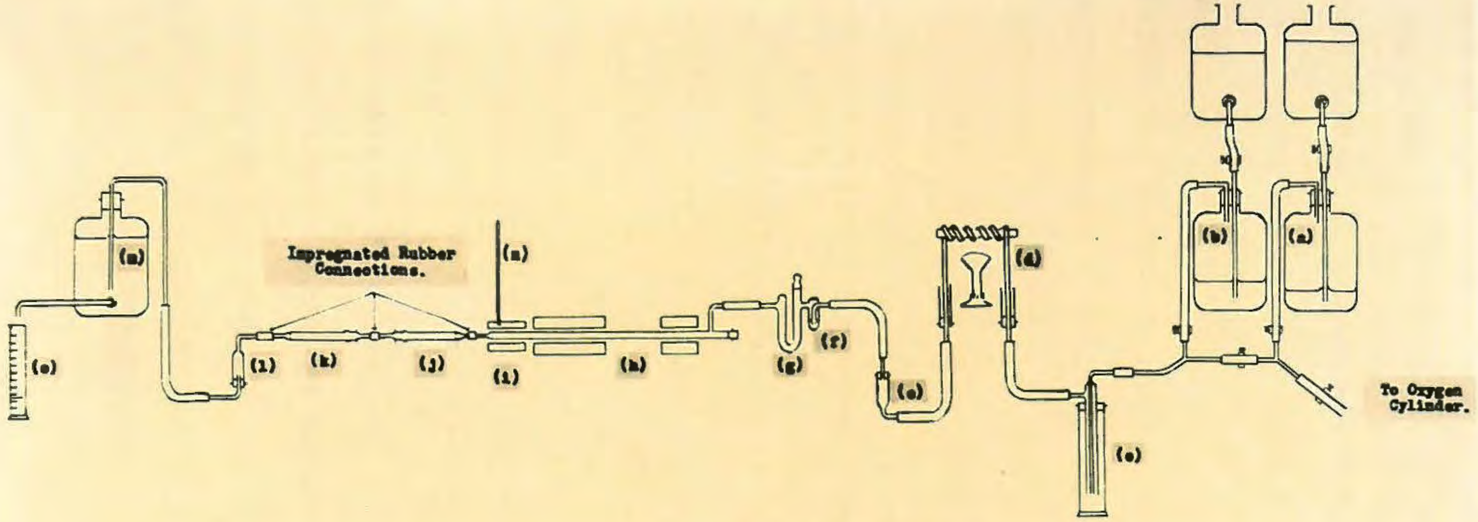
6. APPENDIX.

MICROCOMUBSTIONS

One of the noteworthy advances in Chemistry has been the introduction of methods and techniques permitting the analysis of smaller amounts of substance than commonly used, a fact well recognised in chemical research, both organic and inorganic. In the fields of hormone and vitamin chemistry the application of micromethods has become a necessity.

It was in 1911 that Pregl revolutionized most of the existing macrochemical methods in quantitative organic analysis of pure organic compounds by the introduction of equivalent micromethods. These precedures permitted determinations with samples amounting to a few milligrams and involved not only the handling but also the design of the apparatus. In the subsequent widespread use of Pregl's microanalytical methods for pure organic compounds, the saving in material and time were the decisive contributing factors. The practical applications were an additional advantage which gradually led to the complete replacement of the corresponding macromethods.

Today Pregl's milligram processes have been introduced into both industrial organic research laboratories and the teaching curricula of institutions offering advanced chemical instruction.



COMBUSTION TRAIN.

(a) Oxygen Tank, (b) Air Tank, (c) Pressure Regulator, (d) Preheater, (e) Anhydrone Tube, (f) Bubble Counter, (g) Drying Tube, (h) Electric Furnaces and Combustion Tube, (i) Heating Mortar, (j) Water-Absorption Tube, (k) Carbon Dioxide-Absorption Tube, (l) Drier-Anhydrone, (m) Mariotte Flask, (n) Thermometer, (o) Measuring Cylinder.

APPARATUS

In conjunction with Mr. J.R. Parrish, B.Sc., Hons., this apparatus was set up.

In this apparatus an oxygen (a) and air (b) supply were used and were connected to a pressure regulator (c) as designed by Pregl (96). Traces of organic matter and hydrogen found in many sources of oxygen and air were eliminated by passing the gas through a preheater (d) devised by MacNeven and Clark (97). It consisted of a simple copper spiral with water containers at each end so as to protect the rubber attachments from heat. The preheater was heated with a bunsen burner plus fish tail and by cooling the oxygen and air the possible decomposition of the rubber connections was avoided. The preheater was connected to an anhydrone absorption tube (e) which removed the water, preventing dilution of the concentrated sulphuric acid in the bubble counter.

The bubble counter (f) and absorption tube (g) containing anhydrone and ascarite to remove last traces of water and carbon dioxide respectively, were larger than those used by Pregl (96) and was attached to the side arm of the combustion tube.

The combustion tube (h) was of quartz, 64-65 cms. long, with a side arm (98) of the same dimensions as the arm of the bubble counter. The tube was filled with the "Combination Filling" devised by Niederl and Niederl (99) and closed by a tight fitting cork, removable for the introduction of the sample without disconnecting the air or oxygen stream.

A small constant temperature furnace (i) was used for heating the lead peroxide and the thermometer (n) recorded a temperature of 180°C.

Pregl absorption tubes with a hollow ground glass stopper were used. The water absorption tube (j) was filled with anhydrone with thick glass wool plugs at each end and the ground glass stopper sealed in with Krönigs glass cement. The carbon dioxide absorption tube (k) contained 25 mm. layer of anhydrone followed by ascarite. Glass wool plugs were used at the ends and also between the anhydrone and the ascarite layers. They were connected head to head, the water absorption tube next to the combustion tube, with specially impregnated seamless rubber tubing.

A drier (l), filled with anhydrone, was attached to the absorption tubes from one end while the other was connected to a Mariotte flask (m) as designed by Pregl (96).

The measuring cylinder (o) was to regulate the flow of air and oxygen through the apparatus and the rate of flow was from 4-5 ml. per minute.

The rubber tubing was treated as recommended by Pregl (96) by immersing the tubing in 50% potassium hydroxide at 60°C. for 4 hours and then steaming out for another 2 hours. The pieces of tubber tubing which were impregnated with paraffin wax have specific dimensions (96) and the impregnation was carried out by placing them in molten paraffin wax in a small flask which was evacuated on the suction pump while still warm. As soon as the contents ceased to foam the vacuum was broken to admit the air which forced the paraffin into the pores of the rubber tubing. This procedure of boiling and evacuating was repeated several times until no further rising of bubbles was observed. The paraffin wax was permitted to drain off while still warm and the pieces of rubber tubing were wiped clean on the outside with a clean cloth and the bore with tufts of cotton moistened with a little benzene and finally with dry cotton. These impregnated rubber connections were clearly marked to indicate their respective positions and were always used in that position. When the absorption tubes were not in use the ends were stoppered with a small piece of impregnated rubber tubing containing a glass rod at one end in order to prevent the absorption of carbon dioxide and water from the air.

Whenever the absorption tubes were filled with fresh reagents a combustion was performed with oxalic acid in order to standardise the conditions in the tubes.

PROCEDURE

(1) The main furnace and the constant temperature furnace were switched on and the preheater heated. The temperature of the main furnace was set at about 800° by means of pyrometer.

(2) The capillary ends of the ascarite tube were cleaned with a pipe cleaner and the tube was wiped according to Pregl's directions with a moist cloth, then a moist chamois followed by a dry chamois. It was then placed on the rack for 5 minutes, transferred to the balance by means of a special fork (96) and weighed five minutes later. The anhydrone tube was wiped and weighed in the same way.

(3) The absorption tubes were connected head to head by an impregnated rubber tube 3 cms. long, another 2 cms. long being attached to the anhydrone tube. The absorption tubes were then attached to the combustion train, the anhydrone tube adjoining the latter and the ascarite tube next to the drier of the Mariotte flask, the side arm of which was vertical.

(4) The rubber stopper of the combustion tube was removed, the weighed substance, in a platinum boat, was quickly introduced to within about 5 cms. of the combination filling and the tube immediately closed.

(5) The small furnace and air were switched on and Mariotte flask's side arm pushed horizontal and the flow of water from it was regulated to 4-5 ml. per minute. The small furnace, after it had acquired a temperature of 800° was gradually moved towards the sample. When the sample was reached the air was switched off and the oxygen sent through. The furnace was still moved up until it touched the main furnace and the combustion proceeded with the furnaces in this position. The combustion was carried out with 40 ml. of air and 80 ml. of oxygen and took about 30 minutes.

(6) The absorption tubes were removed and weighed as before. The small furnace and oxygen switched off.

(7) The end of the combustion tube was stoppered with some impregnated rubber tubing, with a glass rod in the other end.

The procedure given was standardised by combusting dried A.R. benzoic acid. It was found that the carbon results were good but those for hydrogen were high. All possible precautions were taken to try and prevent this (96, 99) and blanks were performed. Only the corrected results were recorded in the thesis.

From the corrected results obtained for benzoic acid the probable error of a single reading and of the mean has been calculated.

CARBON

%C	di	di^2
69.20	.193	.03725
68.59	-.417	.1739
68.90	-.107	.01145
69.12	.113	.01277
69.02	.013	.0001690
68.85	.157	.02465
69.18	.173	.02993
69.61	.603	.3636
69.40	.493	.2430
69.33	.323	.1043
69.23	.223	.04973
68.48	-.527	.2777
68.11	-.897	.8046
69.20	+.193	.03725
69.14	+.133	.01769
68.72	-.287	.08237
Mean 69.007		

$$\sum di^2 = 2.2704$$

$$\sqrt{\sum di^2} = 1.507$$

Probable error of single reading =

$$\frac{\sqrt{\sum di^2} \quad .6745}{\sqrt{n-1}}$$

where n = number of results
di = the deviation

but $\frac{.6745}{\sqrt{n-1}} = .1742$

Probable error of single reading =

$1.507 \times .1742$
$= .2625$

Probable error of mean =

$$\frac{\sqrt{\sum di^2} \times .1742}{\sqrt{n}}$$

$= .06562$

HYDROGEN

%H	di	di^2
5.230	.102	.01040
5.196	.068	.004624
4.894	-.234	.05476
5.168	.040	.00160
5.015	-.013	.000169
4.913	-.215	.04623
5.015	-.113	.01277
5.257	.129	.01664
5.241	.113	.01277
5.143	.015	.000225
5.268	.140	.01960
5.196	.066	.004356
4.915	-.213	.04537
5.244	-.116	.01346
5.103	-.025	.000625
5.242	.114	.0130
Mean 5.128		

$$\sum di^2 = .25361$$

$$\sqrt{\sum di^2} = .5036$$

Probable error of single reading

$$= .5036 \times .1742$$

$$= \underline{\underline{.08772}}$$

Probable error of mean

$$= \frac{.08772}{4}$$

$$= \underline{\underline{.02193}}$$

7. EXPERIMENTAL INDEX.

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