# THE ACTION OF SULPHURIC ACID ON CERTAIN ARALKYL ETHERS AND ALCOHOLS.

by

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# ABBREVIATIONS FOR TITLES OF JOURNALS.

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|---|---|
| Annalen, | J. Liebig's Annalen der Chemie. |
| Ber., | Berichte der deutschen chemischen Gesellschaft. |
| Bull. Soc. Chim., | Bulletin de la Société chimique de France. |
| Chem. Abs., | Chemical Abstracts. |
| Chem. Rev., | Chemical Reviews. |
| Chem. Zentr., | Chemisches Zentralblatt. |
| Compt. rend., | Comptes rendus des Séances de l'Académie. |
| Gazz., | Gazzetta chimica italiana |
| Helv. chim. acta. | Helvetica chimica acta. |
| J. Amer. Chem. Soc., | Journal of the American Chemical Society. |
| J.C.S., | Journal of the Chemical Society. |
| J. Russ. Phys. Chem. Soc., | Journal of the Physical and Chemical Society of Russia. |
| Rec. trav. chim., | Recueil des travaux chimiques des Pays-Bas. |
| Z. Electrochem. angew. physik. chem., | Zeitschrift für Electrochemie und angewandte physikalische Chemie. |

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## Introduction.

## Survey of Literature.

# INTRODUCTION.

One of the standard methods for the preparation of aliphatic ethers is by the action of sulphuric acid on the corresponding alcohols, but in the aromatic series, etherification of alcohols takes place more readily. In general, the action of dehydrating agents, such as boric anhydride and zinc chloride, which are less vigorous than sulphuric acid, is sufficient to bring about the formation of an ether from the corresponding aromatic alcohol.

When aromatic alcohols are treated with concentrated sulphuric acid, it is found, as shown hereafter, that condensation of the alcohol by dehydration takes place, yielding either an oily product or an amorphous solid, depending on the conditions under which the reaction is carried out. It is also found that the same product as was formed by the action of sulphuric acid on an aromatic alcohol, can be obtained from the corresponding ether under the same conditions.

This reaction has not hitherto been described in the chemical literature as characteristic of aryl alcohols and ethers, although mention has been made of a reaction of this nature during the course of other preparations. In none of these cases was the constitution of the products investigated and the substances obtained were dismissed as by-products of the reaction under examination.

During the course of this research, a paper published by Wagner-Jauregg and Griesshaber (Ber., 1937,70,3), reported the formation of a condensation product by the action of phosphorus pentoxide and dibenzyl ether in chloroform solution. These authors conclude that this product is formed by the dehydrating action of the phosphorus pentoxide, which causes/

causes condensation of the dibenzyl ether, yielding a substance to which they assign the formula $(C_7H_7)_x$. This reaction of dibenzyl ether with phosphorus pentoxide closely resembles that with sulphuric acid, and is of interest since it constitutes the only reference in the literature to the action of a dehydrating agent on an aryl ether.

The nature of the product formed by the action of sulphuric acid on aryl alcohols and ethers is a matter of general interest. This investigation, however, was carried out with particular reference to the product from dibenzyl ether, obtained in the manufacture of benzyl cellulose, as carried out by Imperial Chemical Industries, Ltd. In the laboratory this substance can be prepared most conveniently by the addition of dibenzyl ether to 80% acid at 140° with efficient agitation. The same product is formed by benzyl alcohol under these conditions.

This thesis deals principally with the formation of this compound and the methods adopted in an attempt to determine its constitution. The compound on purification, is a white amorphous powder which contains carbon, hydrogen and oxygen, but no sulphur. As a result the only reaction by which it can be formed involved the removal of the elements of water between the oxygen of the ether or the alcoholic group and hydrogen atoms from adjacent benzene nuclei or methylene linkages, in the presence of the strong dehydrating agent, sulphuric acid.

This work was also extended to include the substituted aryl alcohols, and from these reactions much interesting data was collected. Varying results were obtained with these alcohols and it would appear that the composition of the reaction products depends mainly on the directing influence/

influence of the substituent groups in the molecule.

The preparation of the condensation products of several aryl alcohols and ethers, their analysis, and properties constitutes the first section of this thesis, while the second part contains an account of the methods adopted in order to determine their constitution, chiefly by the attempted synthesis of the product formed by the action of 80% sulphuric acid on dibenzyl ether.

# SURVEY OF LITERATURE.

# SUMMARY.

This survey of the literature has been divided into several sections, each of which describes the work of various authors on subjects related to the problem under investigation. The chemical literature does not contain many references to reactions analogous with that of benzyl alcohol or dibenzyl ether with sulphuric acid. Such references are found chiefly in the work of Basler and Mettler (see page 5) who prepared diphenylmethane and its derivatives by the reaction of aryl alcohols and certain aromatic hydrocarbons in the presence of sulphuric acid. Only in very few cases did these authors describe the formation of an oily by-product such as would have been formed by the direct action of sulphuric acid and the aryl alcohol. The preparation of diphenylmethane and its derivatives, however, was carried out under special conditions, the aryl alcohol being added to a cold mixture of the aromatic hydrocarbon and sulphuric acid which had been diluted with glacial acetic acid. In addition to sulphuric acid, various other dehydrating agents were used in these condensations, and the resulting compounds are also described in this section.

Apart from these reactions involving aryl alcohols, aromatic hydrocarbons, and dehydrating agents the only other reference to previous work analogous to the reaction of sulphuric acid, and aryl alcohols, is contained in a paper by Wagner-Jeuregg and Griesshaber (loc.cit) which was published during the course of this research. By the action of phosphorus pentoxide on dibenzyl ether in chloroform solution, these authors obtained a product to which they assigned the formula $(C_7H_7)_x$, and in view of the similarity of this reaction with that under investigation, this work is discussed in detail/

detail. In the other sections of this survey, an account is given of several different subjects, which, although not directly connected with the problem of this thesis, are helpful in elucidating the nature of the reaction product, and also in devising a mechanism for the reaction of aryl alcohols and sulphuric acid.

The formation of condensation products by benzyl chloride and its related compounds with the elimination of hydrochloric acid bears a marked resemblance to this reaction by which benzyl alcohol condenses by dehydration in the presence of concentrated sulphuric acid. Jacobsen (see page 14), who studied the condensation of benzyl chloride in the presence of anhydrous aluminium chloride, states that two isomeric compounds of empirical formula ($C_7H_6$) are obtained, the one a soluble resin consisting of hydrocarbon chains containing the group $-CH_2-$, the other an insoluble polymer whose properties could only be explained by assuming a "three dimensional" structure as in Bakelite C.

The mechanism of cyclization affords a theory by which the reaction of aryl alcohols and sulphuric acid may be explained, and in order that this hypothesis may be discussed, Bogert's work on the cyclization of phenylated alcohols is described in the next section (see page 19 ). Bogert and his co-workers conclude from their researches that the main course of such a ring-closure was first the dehydration of the alcohol to an olefine, and then the rearrangement of the olefine by cyclization. The alcohols examined by these authors were of the general formula $Ar. CH_2....CH_2OH$, and the work is of interest because it proves that the formation of an olefine is a definite stage in the dehydration of alcohols of this type.

The final section in this literature survey gives an/

an account of the theories which have been put forward to explain the splitting and rearrangement of benzyl aryl ethers. The earlier hypotheses depend on the presence of a rearranging agent, such as zinc chloride in the reaction mixture, but these have been largely discounted by the work of Behaghel and Freiensehner (see page 25) who discovered that the rearrangement of these ethers takes place by the action of heat alone, although the speed of the reaction is materially assisted by the presence of the metals, zinc or copper. Hickinbottom has recently offered a satisfactory explanation of these observations by assuming that the preliminary phase in the rearrangement is the elimination of the migrating group as a free radical. By means of this work, it is possible to devise a mechanism which explains the formation of the same compound by the action of sulphuric acid with both aryl alcohols and aryl ethers.

## REACTIONS INVOLVING ARYL ALCOHOLS AND DEHYDRATING AGENTS.

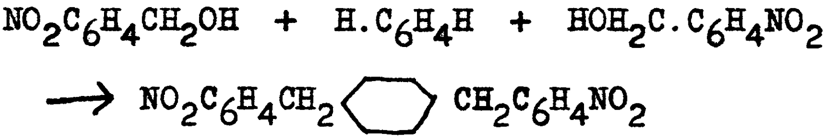
Unlike the corresponding aliphatic alcohols, the etherification of aryl alcohols takes place even in the presence of a mild dehydrating agent, and as has already been stated, the addition of a strong dehydrating agent, such as sulphuric acid, to these alcohols, usually causes the formation of complex condensation products. It has been established by Oddo that the etherification of benzyl alcohol takes place by the addition of a single drop of concentrated sulphuric acid (Gazz., 1909, 1, 31). For the preparation of pure specimens of ethers from the corresponding alcohol, Errera (Gazz., 1918, 18, 240) recommends the use of zinc chloride in preference to sulphuric acid, and states that the use of concentrated sulphuric acid caused the formation of oily by-products. In this connection it is interesting to note that no evidence could be obtained which would indicate that sulphonation had taken place.

Apart from the work of Wagner-Jauregg and Griesshaber, which will be described in a later section (see page 10 ) there are no references in the chemical literature to the direct action of an aryl alcohol or ether with a dehydrating agent. Aryl alcohols, however, have been condensed with aromatic hydrocarbon in the presence of various dehydrating agents, the chief use of such a reaction being in the preparation of diphenylmethane and its derivatives.

Sulphuric Acid:- Meyer and Winster (Ber., 1876, 6, 964) describe a method for the preparation of diphenylmethane which consists in the addition of benzyl alcohol to a mixture of benzene and sulphuric acid. The reaction mixture/

mixture was diluted with glacial acetic acid, and these authors report that under these conditions they obtained diphenylmethane in good yield. This preparation shows that the action between benzyl alcohol and the sulphuric acid had been inhibited by the preferential removal of the elements of water from the alcoholic group and the free benzene nucleus. This selective action was probably caused by the dilution of the sulphuric acid by glacial acetic acid and by the low temperature at which the condensation was carried out.

Becker (Ber., 1882, <u>15</u>, 2091) has applied this method to the formation of substituted hydrocarbons by using m-nitrobenzyl alcohol, and Basler (Ber., 1883, <u>16</u>, 2715) extended this reaction to include p-nitrobenzyl alcohol. Basler postulates the theory that the positions in the benzene nucleus from which the hydrogen atoms are eliminated are "para" to one another, giving a compound according to the following equation:-



Gattermann (Ber., 1893, <u>26</u>, 2811) has also investigated this reaction, and states that in addition to di(p-nitrobenzyl) benzene, p-nitrodiphenylmethane, a condensation product containing only one molecule of p-nitrobenzyl alcohol was also formed:-

$$NO_2C_6H_4CH_2OH + H.C_6H_5 \rightarrow NO_2C_6H_4CH_2C_6H_5$$

No mention is made in any of these preparations of the separation of an insoluble product from the reaction mixture, and from this it would appear that the condensation of these alcohols with benzene takes place more readily than the/

the inter-molecular condensation which is at present being investigated.

Analogous reactions to that with benzene have also been described by Gattermann (Ber. 1894, 27, 2293) involving the use of o- and p-nitrotoluene. It is interesting to note that only one molecule of the aryl alcohol condensed with these nitro-hydrocarbons, and that in neither case was the methyl group involved in the condensation, the orientation of the product depending on the nature of the substituent group in the benzene nucleus containing the alcoholic group.

Similar condensations have also been carried out with p-aminobenzyl alcohol (Gattermann, Ber., 1893, 26, 2816), but no such condensations have been described using o-nitrobenzyl alcohol or with the halogen substituted benzyl alcohols.

Noetling (Ber., 1891, 24, 3127; 24, 3136) has used sulphuric acid as a condensing agent in the preparation of dyestuffs containing the triphenylmethane group, using p-toluidine and nitro-substituted intermediates.

The only other references to reactions in which the aryl alcohols and sulphuric acid were present in the same mixture, were found in the preparation of these alcohols by electrolytic methods (Mettler, Ber. 1905, 38, 1747). This preparation usually consisted in the formation of the alcohol by the reduction of the corresponding acid in a cathode electrolyte consisting of a mixture of ethyl alcohol and sulphuric acid in the ratio 1:1. When the temperature was kept low, the reduction of benzoic acid to benzyl alcohol took place in 80% yield, and this concentration of sulphuric acid was not sufficient to cause inter-molecular condensation of the newly-formed alcohol.

The preparation of substituted benzyl alcohols was also/

also carried out by Mettler using this reduction method, although the yields obtained were always small. With the halogen-substituted benzyl alcohols, frequent mention is made of the oily by-products, which may have been formed by the action of these alcohols and the sulphuric acid of the electrolyte, but Mettler did not investigate the nature of these products.

p-Bromobenzyl alcohol was not prepared by this method, due to the excessive formation of an oily product, presumably by the dehydrating action of the sulphuric acid. O-Nitrobenzyl alcohol, on the other hand was obtained by the electrolytic oxidation of o-nitrotoluene in a mixture of 90% sulphuric acid and acetic acid (Pierron, Bull. Soc. Chim., (3), 25, 853).

In addition to sulphuric acid several other dehydrating agents have been used in the condensation of aromatic alcohols with aromatic hydrocarbons to form derivatives of di- and tri-phenylmethane.

Phosphorus pentoxide. The most powerful of these dehydrating agents is phosphorus pentoxide, which was used in a similar manner to sulphuric acid in the preparation of diphenylmethane (Hemilian, Ber., 1874, 7, 1203). The action was carried out by heating a mixture of benzene and benzyl alcohol with phosphorus pentoxide under reflux, the chief product being diphenylmethane together with a small amount of triphenylmethane.

Nametkin and Kursanoo (J. Russ. Phys. Chem. Soc. 1928, 60, 917, Chem. Abs., 1929, 23, 2162) have also investigated this reaction and these authors report that in addition to diphenylmethane, p-(dibenzyl) benzene is formed by the condensation of a second molecule of benzyl alcohol.

$C_6H_5.CH_2OH + C_6H_6 \rightarrow C_6H_5CH_2C_6H_5$ Diphenylmethane.

$CH_2(C_6H_5)_2 + HOH_2C.C_6H_5 \rightarrow C_6H_4(CH_2C_6H_5)_2$ p-Dibenzylbenzene.

A residue consisting of an oily substance was not examined by these workers. The use of phosphorus pentoxide as a condensing agent was described by Michael and Jeanprêtre (Ber., 1892, 25, 1615) in reactions involving the elimination of water between a carbinol and an aromatic hydrocarbon; this dehydration took place readily without the formation of complex condensation products.

Zinc Chloride. Anhydrous zinc chloride has also found use as a dehydrating agent in reactions involving the condensation of primary alcohol. (Fischer and Rose, Ber. 1880, 13, 674; Kippenburg, Ber., 1897, 30, 1140). The preparation of benzyl phenol takes place readily by heating a mixture of benzyl alcohol and phenol in the presence of anhydrous zinc chloride. This reagent, however, is chiefly used in the preparation of the aromatic ethers from the corresponding primary alcohol (Errera, Gazz., 1918, 18, 240).

Aluminium Chloride. Anhydrous aluminium chloride, besides finding extensive use as a catalyst in the Friedel and Crafts reaction, also acts as a dehydrating agent, e.g. the preparation of diphenyl ether can be carried out by heating phenol and aluminium chloride in the correct proportions. Similar actions depending on the dehydrating action of this reagent are mentioned frequently in the literature (Scholl and Seer, Ann. 1913, 394, 119; Graebe, Ber., 1901, 34, 1778; Frankforter and Kritcheosky, J. Amer. Chem. Soc., 1914, 36, 1511, etc.) There was no record of the dehydrating action of aluminium chloride on aryl alcohols and aromatic compounds until the subject was examined by Huston and Friedmann (J. Amer. Chem. Soc. 1916, 38, 2527; 1918/

1918, 40, 787). When benzyl alcohol was mixed with a little more than the molecular equivalent of benzene and the mixture treated with aluminium chloride, a vigorous action set in with the evolution of heat. Diphenylmethane was the chief product, but small amounts of o- and p-dibenzylbenzene were also isolated, together with a high-boiling compound to which the formular $C_{27}H_{24}$ was given. Further investigation of this compound was promised by these authors in the first paper, but no mention of it was made in their subsequent publications on this subject.

Numerous other dehydrating agents, such as concentrated hydrochloric acid (Suais, Bull. Soc. Chim., (3) 17, 517) and boric anhydride (Noetling, Ber., 1891, 24, 553) have been used in reactions involving primary alcohols. Stannic chloride (Bistizyski, Ber., 1904, 37, 659) has been employed in the preparation of diphenyltolylmethane from benzyl alcohol and toluene.

## THE REACTION OF PHOSPHORUS PENTOXIDE AND DIBENZYL ETHER.

One of the few references to reactions involving the use of dibenzyl either is contained in a paper published by Wagner-Jauregg and Griesshaber (Ber., 1937, 70, 3) during the course of this research. These authors heated equi-molecular quantities of dibenzyl ether and phosphorus pentoxide under reflux in chloroform, and found that only a small amount of the original substance could be recovered. The compound obtained is described as a "polymer", but since analysis shows that it contains no oxygen, the term is incorrect; however as in the section on the condensation products of benzyl chloride (see page 14 ), the word "polymer" has been retained for the sake of continuity.

When dibenzyl ether was heated with phosphorus pentoxide in chloroform, the only visible indications of reaction were the yellow colour of the solution and a strong blue fluorescence. From the chloroform solution a yellowish amorphous substance containing 1-2% of phosphorus, was precipitated with petroleum ether. The removal of the impurity containing the phosphorus was effected by heating a toluene solution of the compound with metallic sodium, and the determination of the molecular weight in camphor gave a value of about 920, thus showing that five mols. of dibenzyl ether are involved in the reaction.

Wagner-Jauregg and Griesshaber state that the fact that the compound obtained was a mixture of different substances was shown by treatment of its benzene solution with alumina; by this means the fraction containing the phosphorus was absorbed and from the benzene solution after washing successively with warm caustic soda, hydrochloric acid and water, a product of the empirical formula $C_7H_7$ was obtained.

By dry distillation of the polymer, a yellow oil was collected/

collected, from which terphenyl was isolated in small quantities.

These authors discussed briefly the formation of an amorphous compound of the approximate formula $(C_7H_6)_x$, and referred to the production of a hydrocarbon, to which this formula was assigned, when benzyl ethyl ether was heated for an hour with thionyl chloride in the presence of stannic chloride (Goldfarg and Smorgonski, Ber., 1936, 69, 1036). A similar polymeric hydrocarbon has been formed by the action of benzyl alcohol with metallic oxides at high temperature, as well as by the polymerisation of stilbene with aluminium chloride in the presence of carbon disulphide. On the other hand they do not mention the better known reaction by which a product of this formula can be obtained, i.e. by the action of aluminium chloride on benzyl chloride (see page 15). Without further preamble they conclude that the description of the properties of the products obtained by these reactions, of which only few details are given in the literature, established that they were similar to that formed by the action of phosphorus pentoxide on dibenzyl ether. In spite of their conclusions, these authors compared the experimental figures for the final analysis of the product after purification, with the theoretical values for a hydrocarbon with the formula $(C_7H_7)_x$. In this connection it is difficult to see how they can formulate a scheme of reaction by which the compound $(C_7H_7)_x$ could be formed from dibenzyl ether, $C_{14}H_{14}O$, by the removal of the elements of water, no matter how many molecules of the ether were involved in the reaction.

In view of the similarity of this work to the action of dibenzyl ether and sulphuric acid, the experimental part of this investigation was repeated by the author (W.G.C.) Following the method of Wagner-Jeuregg and Griesshaber, it was found that the product obtained by boiling dibenzyl ether with/

with phosphorus pentoxide in chloroform for 12 hours was very viscous and did not solidify even after repeated precipitation from chloroform with petroleum ether. Also it was noticed that during the reaction, the product was not completely dissolved by the chloroform, but that the greater part of it floated in the reaction liquid as an oily mass, in which was occluded much of the solid phosphorus pentoxide. As a result of these observations, the reaction vessel was fitted with a mechanical stirrer and the mixture was kept agitated continuously during the experiment. This served to keep the dibenzyl ether and phosphorus pentoxide in intimate contact by forming an emulsion of the chloroform solution of the ether with the phosphorus pentoxide. On precipitating the product from chloroform with petroleum ether, no difficulties were experienced in obtaining a solid from the oily deposit after this treatment.

The dry distillation of this product was carried out as described by Wagner-Jauregg and Griesshaber. These authors report that by heating in a distilling flask, a water clear liquid was collected between 190° and 250°, and about 250° a thick reddish yellow oil started to distil into the receiver. This oily distillation product was taken up in alcohol, and the substance precipitated by cooling in ice. The colourless crystals obtained were identified as terphenyl, M.P. 205-206°.

When this dry distillation was attempted, no distillate could be obtained even when the temperature was raised to 250°. Further increases in temperature only resulted in the charring of the product.

As it was possible that the distillate, which may have been formed, was being returned to the flask by a slow current of nitrogen was passed through the molten liquid in order/

order to drive over any condensible vapours. A retort was also used in place of a distilling flask, and after heating the product for 2 hours at 200, the temperature was slowly raised to 250°, and a few drops of a clear liquid began to distil. This temperature was maintained for another hour, but no further distillate was collected. When the temperature was increased to 300°, no yellowish oil, such as was described by Wagner-Jauregg and Griesshaber, was obtained, and prolonged heating above this range caused complete decomposition of the substance in the retort.

These authors reported that by this dry distillation, they isolated a product which they have shown to be terphenyl. The distillate from which this was obtained, was collected at 250°, whilst the boiling point of terphenyl recorded by Beilstein, is 380°, i.e. the thick reddish yellow oil distilled 130° below the boiling point of terphenyl. In view of this fact and the difficulties encountered by the author when an attempt was made to repeat this dry distillation, the isolation of terphenyl from the reaction product of dibenzyl ether and phosphorus pentoxide by this method, must be accepted only with reserve.

This paper by Wagner-Jauregg and Griesshaber was published after the author had begun his investigation of the reaction of dibenzyl ether and sulphuric acid and any apparent duplication of the work which follows is explained by this fact. From this summary, however, it will be seen that whilst there is a similarity in the actions of phosphorus pentoxide and sulphuric acid with dibenzyl ether, there is the essential difference that the product from sulphuric acid still contains a small percentage of oxygen

## CONDENSATION PRODUCTS FROM BENZYL CHLORIDE AND RELATED COMPOUNDS.

The formation of an insoluble hydrocarbon by the action of aluminium chloride on benzyl chloride was observed many years ago by Friedel and Crafts (Bull. Soc. Chim. 1885, 43, 53). In the same year Gladstone and Tribe (J.C.S., 1885, 47, 448) obtained a similar substance from benzyl chloride by the action of a copper-zinc couple, and frequent mention is made of the formation of related substances in the preparation of aromatic hydrocarbons by the Friedel and Crafts reaction (Schramm., Ber., 1893, 26, 1706; Lavoux and Lombard, Bull. Soc. Chim., 1895 (4), 7, 541; Meunier, C. r., 1893, 137, 714). The unsatisfactory yields in this type of reaction involving the use of benzyl chloride, were greatly improved by Radziewanoski (Ber. 1894, 27, 3237) who discovered that by the use of a large excess of the other constituent in the reaction, the formation of this insoluble substance was greatly minimised, e.g. in the preparation of diphenylmethane, a large excess of benzene prevented the separation of the complex $(C_7H_6)_x$ which was formed by benzyl chloride. Radiewanoski explained this by means of the following equation:-

$$(C_6H_4{:}CH_2)_2 \ + \ x\ C_6H_6 \longrightarrow x\ C_6H_5CH_2C_6H_5$$

Little information is available regarding the nature and properties of these compounds; insoluble amorphous substances have sometimes been obtained, while in other cases the products have been soluble resins, yet the experimental conditions pertinent to the formation of one or the other have not been defined.

This work was undertaken by Jacobsen (J. Amer. Chem. Soc., 1932, 54, 1513) as part of a general study of polymeric substances. The term polymer cannot be correctly applied to the compounds under review, since their formation takes place by inter-molecular condensation with the elimination in most/

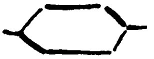
most cases of the elements of hydrochloric acid, but in order to report the work more consistently, Jacobsen's phraseology has been retained.

Jacobsen found that when benzyl chloride was polymerised by the action of aluminium chloride, two products were obtained in varying amounts depending on the experimental conditions. One of these was an infusible, insoluble amorphous solid, and the other a soluble brown resin which softened and melted at 70-85°. The latter was soluble in all proportions in chloroform, carbon disulphide and aromatic hydrocarbons, but insoluble in alcohols and ketones. Molecular weight determinations in benzene by the ebullioscopic method gave for different lots of the soluble resins, values varying from 1260 to 2250.

Only very small amounts of aluminium chloride were necessary to bring about this condensation, and under these conditions a mixture of the insoluble amorphous polymer and the soluble resin was obtained. When the quantity of the aluminium chloride was increased, polymerisation occurred more vigorously to yield the insoluble polymer as the main product and only a small quantity of resin. Polymerisation of benzyl chloride can be effected by ferric chloride and stannic chloride, the chief product in these cases being the fusible soluble resin.

Chemically, both the soluble resin and insoluble polymer are hydrocarbons with the empirical formula $C_7H_6$. The only exception was the resin obtained by means of stannic chloride, which contained a small amount of chlorine. Jacobsen considers that in view of the experimental conditions it is surprising that the reaction should produce exclusively materials of high molecular weight. The formation of considerable quantities of 9:10 dihydro-anthracene by the inter-condensation/

inter-condensation of two molecules of benzyl chloride might reasonably be expected especially since such a condensation would involve the formation of a six-membered ring. Wertyporoch and Farnik (Ann., 1931, 491, 265) however have reported the isolation of small quantities of a tolylbenzyl chloride from the action of benzyl chloride and aluminium chloride.

Jacobsen states that the properties of the soluble condensation products can best be accounted for by assuming that they are hydrocarbon chains containing the group  $CH_2$ - as the structural unit. It is likely that coupling occurs mainly in the position para to the methylene group, since the para isomer is usually obtained in larger amounts than the ortho or meta isomers when the Friedel and Crafts reaction is applied to toluene, diphenyl, and related compounds (Gattermann, Ber., 1897, 30, 1627; Limpricht, Ann., 1900, 312, 92; Huston, J. Amer. Chem. Soc., 1924, 46, 2775). The properties of the insoluble and infusible condensation product can be explained by assuming a "three-dimensional" structure as in the case of Bakelite C. (Carothers, Chem. Reviews 8, 353).

While no information concerning the number of structural units in the hydrocarbon chains of the insoluble polymer could be obtained, the average number of $C_7H_6$ groups in the chain of the soluble resins varied from 14 to 29 as indicated by molecular weight determination. Reliable information concerning the arrangement of the units in the chain could not be secured on account of the high resistance of these products to reagents. Attempts to oxidise the compounds revealed a high degree of stability, such oxidising agents as potassium permanganate and potassium dichromate being/

being without effect. By the action of nitric acid on the soluble condensation product, an infusible resin containing nitrogen was obtained, but the presence of nitro groups could not be established. Chromium trioxide in boilding acetic acid gave products corresponding approximately to the structure $(C_6H_4CO\ C_6H_4CO)_x$. However the presence of ketonic groups could not be demonstrated by the usual methods. The action of bromine upon the soluble resin yielded a product containing one bromine atom for two $C_7H_6$ groups.

The main product from the reaction of aluminium chloride and p-bromo-benzyl chloride in carbon disulphide was an insoluble and infusible polymer. This was accompanied by a small amount of resin similar in solubility characteristics to the benzyl chloride resin. When ferric chloride was used, the entire product was a soluble resin. Both the soluble and insoluble polymers were halogenated hydrocarbons having the empirical formula $C_7H_5B_r$ for which the structural unit would be Br  $CH_2$ -. Molecular weight determinations gave values from 2000 to 2600 indicating that the chains of the soluble resigns averaged from 12 to 15 units. The polymers were not readily attacked by oxidising agents, but bromination of the soluble resins yielded a product with one bromine atom in each benzyl nucleus.

By the action of sodium on p-dibromobenzene and upon p-xylyene bromide, polymeric substances were also obtained. p-Dibromobenzene yielded polymers which consisted of chains made of phenylene groups and terminated at both ends by bromine atoms. From p-xylylene bromide, an infusible and insoluble polymer having the empirical formula $(C_8H_8)_x$ was obtained. From the method of preparation and the properties of/

of the polymer, it is certain that structurally it consists of long chains of $CH_2$  $CH_2$ - groups.

The formation of an amorphous compound of the approximate formula $(C_7H_6)_x$ from benzyl ethyl ether by the action of titanium tetrachloride and thionyl chloride has been described by Goldfort and Smorgonski (Ber., 1936, 69, 1036) and a similar hydrocarbon has been formed by the dehydration of benzyl alcohol with metallic oxides at high temperatures (Sabatier and Mailhe, Compte, rend., 1908, 147, 108).

From these series of polymers it may be concluded that, where a soluble fusible polymer has been formed, the compound consists of long hydrocarbon chains containing the group $C_6H_4\ CH_2$ - as the structural unit, with coupling taking place mainly in the position para to the methylene group. It is of interest to compare these compounds with the products obtained by the action of sulphuric acid and aryl alcohols and ethers.

## CYCLIZATION OF SOME PHENYLATED ALCOHOLS AND RELATED OLEFINES.

In a reaction such as the intermolecular condensation of benzyl alcohol by the removal of the elements of water in the presence of sulphuric acid, one method by which it may take place, consists in the formation of a hydrocarbon chain with subsequent ring-closure to give a cyclic compound. In recent years much work has been done on the cyclodehydration of aromatic alcohols, and although the products obtained by the cyclization of these alcohols do not bear a close resemblance to those at present being studied, this work contributes interesting data which helps to elucidate the constitution of the reaction product from benzyl alcohol and sulphuric acid.

The investigation of the cyclodehydration of aromatic alcohols was chiefly carried out by Bogert and his co-workers (J. Amer. Chem. Soc., 1934, 56, 184, 1935, 57, 151) who describe the cyclization of some simple phenylated alcohols and related olefines, e.g., $\gamma$ phenyl propyl alcohol.

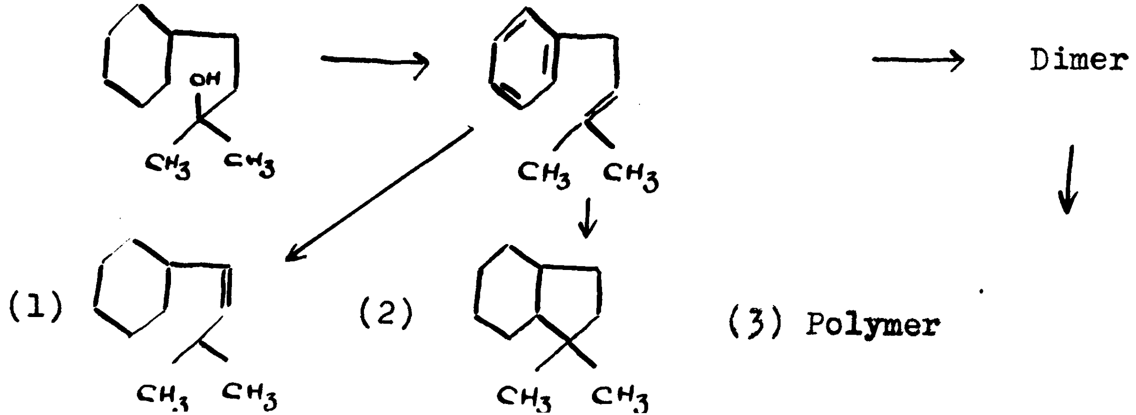
Since the dehydration of an alcohol involved the removal of the alcoholic hydroxyl from its carbon atom together with the hydrogen atom of an adjacent carbon atom, these authors concluded that the ease of dehydration of various alcohols depended on the character of the alcoholic group (primary, secondary or tertiary) and that among alcohols of a given class the relative rates of dehydration of an aralkyl alcohol by sulphuric acid were then determined by the nature of the substituent groups present in the nucleus.

Owing to the oxidising and sulphonating action of hot sulphuric acid, temperatures much above room temperature were not used by these workers to force the dehydration of/

of sluggish alcohols, such as phenyl ethyl carbinol. In this case, as well as in other cases in which it was feared that the condition necessary for the dehydration of the alcohol might be too drastic for the cyclization of the intermediate olefine, recourse was had to the use of phosphoric acid at 230-240°.

From their researches these authors conclude that the main course of the reaction is first the dehydration of the alcohol to an olefine and then the rearrangement of the latter by cyclization, although in a few cases there was evidence that the cyclization was effected by direct condensation of the alcoholic group with the ortho hydrogen of the aromatic nucleus.

In the formation of indanes from γ phenylpropyl alcohols, the first mechanism which suggests itself is direct cyclodehydration, i.e., the elimination of the alcoholic hydroxyl and an ortho nuclear hydrogen as water. Bogert, however, states that the alcohol probably undergoes dehydration to one or more olefines which may then react in three ways (1) rearrangement due to the shift of the double bond (2) cyclization by the migration of an ortho nuclear hydrogen to the double bond with subsequent ring-closure (3) by dimerization and subsequent polymerisation. The formation of the olefine and its subsequent reaction takes place as follows:-



In several cases there is evidence that the olefine is an intermediate in the cyclodehydration. By progressively reducing the strength of the sulphuric acid used, a point was reached where the product was largely olefine, indicating that with stronger acid the olefine was probably an intermediate. By resorting to 85% phosphoric acid these workers showed that olefine was immediately formed by the alcohol and that the cyclic compound was produced subsequently and then only slowly.

The structure of the product obtained by dehydrating a phenylated alcohol was readily determined by bromination and oxidation, the formation of a dibasic acid with potassium permanganate definitely proving the existence of the indane nucleus.

In all cases examined by Bogert and his co-workers, the alcohol which was treated with sulphuric acid was of the general type $X.CH_2.....CH_2OH$, i.e., it always contained a straight side-chain, which consisted of from three to five methylene linkages. The work is of interest, however, because it proves the formation of an olefine to be a definite stage in the dehydration of alcohols of this type.

## The Splitting and Re-arrangement of Benzyl aryl ethers.

As will be shown later, the reaction of benzyl alcohol and dibenzyl ether with sulphuric acid results in the formation of the same product, and this fact may be explained in either of the following ways, (1) by the etherification of benzyl alcohol in the presence of sulphuric acid to give dibenzyl ether, followed by a subsequent reaction with sulphuric acid or (2) by a scission of the dibenzyl ether and re-arrangement of the radicals so formed, when the primary reaction may be regarded as taking place between benzyl alcohol and sulphuric acid. In connection with this later hypothesis it is interesting to examine the references in the literature which deal with the scission and re-arrangement of aryl ethers.

The scission of aryl ethers has been carried out by various methods and one of the most common of such reactions is the formation of substituted hydrocarbons by the treatment of these ethers with the phosphorus pentahalides (Autenreith and Muhlonghaus, Ber., 1906, 39, 4100).

$$\mathrm{Ph.\,O.R.} + \mathrm{PCl_5} = \mathrm{Ph.Cl.} + \mathrm{POCl_3} + \mathrm{R.Cl.}$$

Aryl alkyl ethers can be dealkylated by warming with aluminium chloride, yielding the free phenol (Pfeiffer and Haack, Annalen, 1928, <u>460</u>, 156) and some of these ethers are decomposed by treatment with sodium at high temperatures. The action of sodium on dibenzyl ether was examined by Schorigin (Ber., 1925, <u>58</u>, 2031). When this ether was heated with sodium on a water-bath for several hours, the reaction mixture was found to contain toluene, benzyl alcohol, and phenyl benzyl carbinol.

$$C_6H_5.CH_2\,.\,O\,.\,CH_2.C_6H_5 \longrightarrow C_6H_5CH(OH)CH_2C_6H_5.$$

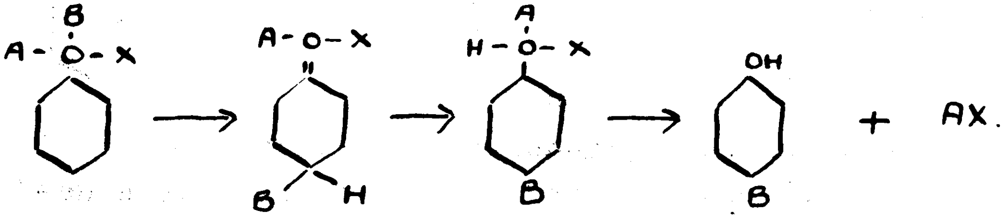
A/

A small amount of benzoic acid was found, and the reason for the production of this acid lies probably in the decomposition of dibenzyl ether which Lowe (Annalen, 1887, 241, 374) observed on distilling at ordinary pressures, when it split into toluene and benzaldehyde.

$$C_6H_5CH_2O.CH_2C_6H_5 \longrightarrow C_6H_5CH_3 + C_6H_5CHO$$

The benzoic acid can then be formed by oxidation or by the Cannizzaro reaction.

The migration of benzyl groups in an aryl ether has been studied by various workers. Van Alphen found that by heating phenyl benzyl ether for one hour at 160° with zinc chloride, it was converted into 4 hydroxydiphenylmethane (Rec. trav. chim., 1927, 46, 799). This migration has been explained by the author with the aid of two hypotheses viz. that the initial action with phenol and phenyl ethers consists of an addition to the oxygen atom and that in this condition, i.e. with a quadrivalent oxygen atom in the molecule, the latter is most prone to atom migration, the following scheme being put forward:-



In this scheme, AX is the re-arranging agent and B the benzyl group.

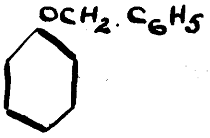
Saturated alkyl phenyl ethers were re-arranged to the corresponding substituted phenols by means of a mixture of concentrated sulphuric acid and glacial acetic acid (Niederl and Natelson, J. Amer. Chem. Soc., 1931, 53, 1928.)

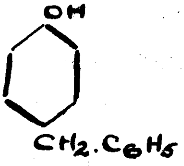
In/

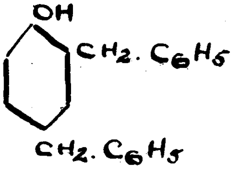
In these experiments on the scission of ethers, various other compounds such as boron fluoride and anhydrous aluminium chloride were used as re-arranging agents. None of these workers, however, have described experiments with dibenzyl ether and in this connection, several experiments were carried out by the author (W.G.C.) using these re-arranging agents mentioned above. In all cases, the dibenzyl ether was unchanged, except for slight decomposition on prolonged heating to give toluene and benzoic acid.

The most important groups which migrate are benzyl, allyl and tertiary alkyl but all the theories which have been put forward to explain this migration require the presence of a re-arranging agent in the reaction mixture. Contrary to these theories, however, Behaghel and Freiensehner found that the formation of the isomeric benzyl - phenols took place by the action of heat alone.

Phenyl benzyl ether was heated for some time at 250° under reflux and from the syrupy product was isolated (1) p-Benzylphenol and (11) 2:4 - Dibenzylphenol.

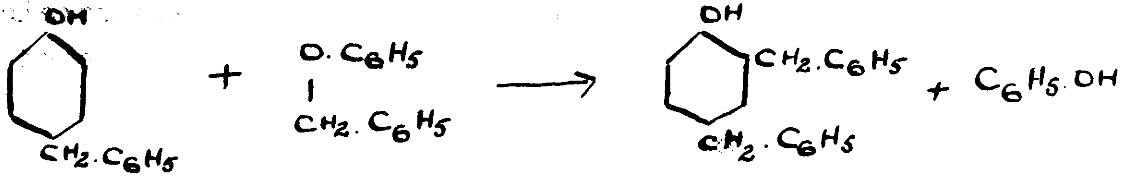






The formation of dibenzylphenol in this reaction has been explained by these authors in the following way:- They consider that it is not necessary that the benzyl group should enter into the particular nucleus to which it was formerly attached. It can well be imagined that the benzyl group would seek another nucleus in its migration from the ethereal oxygen, and so the benzyl nucleus in the ether can migrate not only to the para hydrogen of its own group but also to a benzyl phenol molecule which has been formed in the/

the reaction. The phenyl benzyl ether thus benzylates a molecule of benzyl phenol, forming phenol and 2:4 - dibenzyl phenol, both of which were found in the reaction mixture.



The addition of copper or zinc to the mixture increased the speed of reaction, although the temperature had to be maintained at 250°.

The benzyl ethers of other phenols behaved similarly on being heated, and the presence of zinc or copper again influenced the time of reaction. The migration of the benzyl group took place mainly in the para position to the ethereal linkage, and if this was occupied, as in p-tolylbenzyl ether, the migration either did not take place or only proceeded very slowly. Also, as with β-naphthylbenzyl ether, the migration may occur in the ortho position.

Behaghel and Freiensehner think that the re-arrangement of aryl ethers by the action of heat alone, must be different from these other cases in which a re-arranging agent was used. As a first reaction they consider that intermolecular re-arrangement by the splitting of the ether is most probable, but by whatever mechanism the re-arrangement of these ethers is attempted, all such re-arrangements are limited by the difference in the repulsion energy which exists between the phenyl ether and the isomeric nuclear substituted phenol.

Latimer formed an equation for the repulsion value for the migration of a carbon atom from the ethereal oxygen atom to a nuclear carbon atom and came to the conclusion that such a migration is connected with a loss of repulsion energy/

energy (J. Amer. Chem. Soc., 1929, 51, 3185). From this it would be seen that phenyl benzyl ethers can re-arrange to the isomeric phenols since there is a difference in the repulsion energy, but it would depend on the composition of the ether whether migration is favoured. In the phenyl nucleus the hydrogen atom in the para position and also the ortho hydrogen are influenced so that the benzyl group can easily displace them and therefore one of the preliminary conditions for a re-arrangement has been fulfilled.

The theory of Behaghel and Freiensehner that the re-arrangement of benzylphenyl ethers takes place by the migration of the benzyl group has been supported by the recent work of Hickinbottom (Nature, 1938, 142, 830) who found that if the re-arrangement of these ethers is effected in a suitable solvent, the migrating group is transferred in part to the solvent. Thus by heating a quinoline solution of benzylphenyl ether, benzyl quinoline is formed together with the normal products of the re-arrangement. Toluene is also formed.

Hickinbottom considers that these observations find a satisfactory explanation if the assumption be made that the preliminary phase is the elimination of the migrating group as a free radical. The toluene would result from the disproportionation of the benzyl radical, - a reaction known to occur with free radicals (Hey and Waters, Chem. Rev., 1937, 21, 159). The transference of the migrating group to the solvent arises out of its reaction with the free radical. The assumption that the free radical takes part in the reaction makes clear the observation that the rearrangement of benzyl phenyl ether is very materially assisted by the presence of metals such as zinc or copper.

The/

The references quoted in this section summarise the theories which have been put forward to explain the re-arrangement of aryl ethers, and this work has been used in a later part of the thesis in order to explain the reaction of dibenzyl ether and sulphuric acid.

## Reaction of 80% Sulphuric Acid with Dibenzyl Ether.

I. (a) Standard Method of Preparation.
   (b) Further methods of preparing this product.

II. Molecular Weight Determinations.

III. Reactivity of the Reaction Product.

IV. Derivatives.

V. Chromatographic Adsorption.

## I. (a) STANDARD METHOD OF PREPARATION.

The preparation of the reaction product from dibenzyl ether and 80% sulphuric acid was carried out according to the following method:

86 gms. Dibenzyl ether.
180 ml. Sulphuric acid. S.G. 1.84.
80 ml. water.

The water was poured into a 500 ml. bolt-head flask and when the sulphuric acid was added with mechanical stirring, the temperature rose to 120-130°. The mixture was heated to 140°, and the dibenzyl ether run in at such a rate that the temperature was maintained by the heat of the reaction. This addition usually took from 12-15 minutes, and after it was complete, the temperature was kept at 140° for a further 15 minutes by external heating. The acid mixture was allowed to cool, poured into water, and a solid cake separated out. Yield = 83 gms.

During the preliminary experiments, the product did not separate as a solid, but an oily substance was obtained when the reaction mixture was diluted with water. The nature of this product was considerably improved by the use of efficient agitation. This was best achieved by means of a double-bladed propellor stirrer, with blades opposed to one another, and driven by a high-speed electric motor. It was found also that, if the dibenzyl ether was purified by distillation under reduced pressure immediately before use, the product solidified initially at a much higher temperature. The treatment, however, did not free the ether from benzaldehyde, as it was found by Bennett & Willis that dibenzyl ether suffers/

suffers a slight decomposition in distillation even at temperatures below 200°.

Further purification of this ether was carried out by the method described by Bennett and Willis (in their work) on the use of this solvent in the cryoscopic determinations of molecular weights. (J.C.S. 1928, 2305). Dibenzyl ether in spite of a marked tendency to supercooling, could be induced to crystallise below 0°, and gave a crystalline solid, M.P. 3.6°. The ether after fractional distillation, was cooled in a mixture of ice and hydrochloric acid, and crystallisation usually took place by vigorous stirring at temperatures below - 15°. Above this the liquid often remained for hours in a super-cooled state. After repeated fractional crystallisation, the ether had a faint odour, quite distinct from that of benzaldehyde.

Using this purified ether and the improved method of agitation, the cake from the reaction mixture solidified immediately on being poured into water and was washed free from sulphuric acid by crushing under water. The last traces of acid were removed by treating the crushed cake with dilute alkali, preferably sodium carbonate, and repeated washing alternately by filtration and decantation. The purified product was neutral to litmus, and a test for sulphur by fusing with sodium and adding sodium nitroprusside to the aqueous extract was blank.

## SOLUBILITY.

The dry product was only sparingly soluble in the usual organic solvents, and in those cases where the solubility was more suitable, the substance separated from the solution on cooling as an oil.

The following solvents only dissolved the product very/

very slightly:-

Alcohols and ethers in general, acetone, carbon tetrachloride, carbon disulphide, acetic acid, chlorobenzene, pyridene, anisole, and the higher hydrocarbon solvents. Decalin and tetralin were fairly good solvents at the boiling point, but were not of much practical value owing to their high boiling ranges and the consequent risk of decomposition.

The solvents in which the product dissolved most readily were chloroform, benzene, veratrole and dioxan. Chloroform and benzene, while dissolving the material fairly easily on heating were not suitable for purification and for the purpose of analyses, as the product separated from these solutions as an oil, while veratrole was troublesome owing to its high melting point. It was noticeable with several of the solvents used, particularly chloroform and dioxan, that the solutions showed a blue fluorescence.

The only solvent from which precipitation in the solid state took place was dioxan, and the best results were obtained by the addition of absolute alcohol slowly to the warm solution until it became slightly milky. From this mixture the substance separated as a powder, but no crystals were obtained. Decolourisation was effected by boiling the dioxan solution with Norite, and while the product obtained appeared white, a concentrated solution still retained a faint yellowish brown tinge even after several treatments by this method.

From the first purifications carried out using dioxan a small amount of solid was obtained which gave a melting point 126-127°. When, in later experiments this extensive purification was repeated, a melting point as high as this could not be obtained, even after the purified product had/

had been subjected to intensive drying by allowing it to stand under vacuum in the presence of concentrated sulphuric acid and phosphorus pentoxide for some time. The average melting range found was 93-95°, and this value could be repeated using the standard conditions of the reaction as previously described.

ANALYSES.

Since the test for sulphur on the purified product showed no reaction with sodium nitroprusside, sulphonation had not taken place and the acid had acted only as a dehydrating agent. An estimation of sulphur carried out by the Carius method proved to be blank, showing that no acid remained occluded in the reaction product after this purification. Thus the substance can only contain carbon and hydrogen and oxygen, and any deficiency from the theoretical 100% after the addition of the values for the percentage composition of carbon and hydrogen, must represent the amount of oxygen present. As the figures obtained for these analyses would be of paramount importance in the subsequent work on the determination of the nature of this product, a series of carbon-hydrogen analyses was carried out by the author, and samples of the substance from a series of preparations purified under identical conditions were submitted to several independent analysts. These analyses gave the following results

| | C. | H. | O (by difference |
|---|---|---|---|
| Macro Method | 89.6 | 6.9 | 3.5 |
| (W.G.C.) | 89.7 | 7.0 | 3.3 |
| | 89.45 | 6.75 | 3.8 |
| Hemi-macro Method | 89.5 | 6.8 | 3.7 |
| | 88.4 | 6.7 | 4.9 |
| Micro Method | 89.4 | 6.9 | 3.7 |
| | 88. 5 | 6.9 | 4.6 |
| | 87.70 | 6.80 | 5.5 |
| | 87.1 | 6.90 | 6.0 |

From these analyses it would appear that the product under examination definitely contains oxygen, and taking an average of these results, the simplest structure which can be devised for a substance with such an analysis would have an empirical formula $C_{28}H_{26}O$, and a composition of $C = 88.8\%$, $H = 6.9\%$, and $O = 4.3\%$. Such a compound could be formed by the elimination of the elements of water from two molecules of dibenzyl ether or from four molecules of benzyl alcohol:-

$$4 \times (C_6H_5.\,CH_2OH) - 3H_2O = C_{28}H_{26}O$$

Before further speculation as to the nature of this compound was attempted, determinations of the molecular weight of the product were carried out in a variety of solvents.

## I (b) FURTHER METHODS OF PREPARING THIS REACTION PRODUCT.

Although the complex product under investigation was first prepared by the action of 80% sulphuric acid on dibenzyl ether, it can conveniently be prepared by other methods.

The simplest of these methods is by the use of benzyl alcohol in place of the dibenzyl ether. Using exactly the same conditions as have been previously described for the case of the ether, benzyl alcohol reacted with 80% sulphuric acid at 140$^{o}$ to give a product similar both in melting range and percentage composition. This method of preparation has the advantage that the same precautions are not necessary to avoid the formation of an oily product. This was due to the greater ease of purification of benzyl alcohol over the corresponding ether. Also the instantaneous reaction in the sulphuric acid did not allow time for the dibenzyl ether to decompose to give benzaldehyde which has been shown to have an adverse effect on the course of the action.

Phosphoric acid was used as the dehydrating agent in place of sulphuric acid, the reaction being first attempted with benzyl alcohol as the product usually solidified more readily from this starting material. Using 80% phosphoric acid heated to 190$^{o}$, the reaction product was obtained in a semifluid state. After several modifications, however, the conditions of the reaction were finally established, using 90% phosphoric acid heated to 160$^{o}$. Rapid agitation at 160$^{o}$ was continued for ½ hour after the addition of the benzyl alcohol, and the product from this treatment was identical with/

with that obtained in previous preparations with sulphuric acid. Also unlike the material prepared by Wagner-Jauregg by the action of phosphorus pentoxide on dibenzyl ether in chloroform solution (see page 10), this product contained no phosphorus, as it could all be removed by crushing the crude product under water.

Numerous experiments were carried out with dibenzyl ether and phosphoric acid of varying strengths in order to establish the conditions under which the formation of a solid product took place. The phosphoric acid was dehydrated by heating to 240°, above which temperature the acid became too syrupy for efficient agitation. In the reaction with dibenzyl ether, however, temperatures in excess of 200° were not used, as decomposition of the ether to benzaldehyde took place, and using these reagents no satisfactory products could be obtained.

Since the melting point of the product from 80% sulphuric acid was not sharply defined even after exhaustive purification by various methods, several experiments were carried out in which the strength of the acid and the time and temperature of heating were altered. From these experiments it was found that as the strength of the acid was increased, so the temperature of heating had to be decreased to prevent sulphonation and excessive charring. The products from these reactions were usually much darker in colour than those obtained under the original conditions, and this colour impurity was extremely difficult to remove. The best results were obtained by the replacement of the water in the sulphuric acid by acetic anhydride; using a mixture of 80% sulphuric acid and 20% acetic anhydride heated to 120°, a product was isolated which showed only a trace of the yellowish brown colour which had previously been present, but the melting range of the substance was not appreciably raised, remaining at 90-95°, with an initial softening temperature of 65°.

## II. MOLECULAR WEIGHTS.

Owing to the insoluble nature of the compound, the choice of solvents for molecular weight determinations is very limited. Benzene was first tried as a cryoscopic solvent, but the depression obtained was not sufficiently large to ensure accuracy of the results. A similar difficulty was encountered using the boiling-point method with both benzene and chloroform.

Dioxan was then tried as solvent by the cryoscopic method, using the method described by Anshutz and Broeker (Ber. 1926, 59, 2844). These authors, although they recommend dioxan as a solvent, state that variable results are often obtained due to difficulty of preparing a sufficiently pure sample of the solvent.

The main impurities which are present in dioxan are small amounts of peroxides and water, and to remove these constituents, the following method of purification was adopted. The impure dioxan was boiled under reflux for an hour with solid caustic potash, and then fractionally distilled, only the liquid distilling between 101 and 102 being collected. This distillate was dried over sodium wire for several days until all evolution of gas from the sodium had ceased, and then redistilled over the same range of temperature. In the final distillation only the fraction boiling at 101.5° was collected.

In this purified state the dioxan was very hygroscopic and the melting-point apparatus was completely sealed from the atmosphere by attaching a mercury seal to the stirrer, and closing the side-arm with a rubber stopper. Even with this precaution, fluctuations in the melting-point of/

of the dioxan occurred, and as the solvent has a relatively low molecular constant, the variations were of such an order as to make it impossible to obtain accurate results using this solvent.

Veratrole was then used as a cryoscopic solvent, and in this case also, variations in the values of the molecular weight were encountered due to atmospheric moisture. The use of the mercury seal on the stirring rod partly overcame this difficulty, and the freezing point of veratrole remained constant to within .005°. The results obtained with this solvent were not consistent, but varied with the concentration of the solution used.

| Concentration in gm/ml. | Molecular Weight. |
|---|---|
| .0032 | 376 |
| .0040 | 380 |
| .0042 | 405 |
| .0060 | 479 |

These values suggest that association of the molecules had taken place at higher concentrations, and thus these results were not suitable for the establishment of a molecular formula.

Determinations of the molecular weight by Rast's method in camphor were carried out by Schoeller of Berlin, and this analyst reported values of 598 and 593.

Further estimations were carried out in camphor by the author, by a modification of Rast's method as described as follows:-

The determination was conducted in an ordinary freezing/

freezing point apparatus with a thermometer graduated in 1/10th of a degree on a scale reading between 150° and 200°. The tube was filled to a depth of one inch with liquid paraffin and heated by a bunsen burner with a small flame, which was well protected from draughts.

The camphor was purified by sublimation, and pulverised on a porous plate with a nickel spatula. The capillary tubes used for the melting point determinations were both longer and wider than is usual; they should be at least 10 cms. long and 2-3 mms. in diameter in order to have sufficient semi-molten material in the tube to observe accurately the process of melting. Some of the purified camphor was transferred to a capillary tube, and pressed down firmly into it by means of a second capillary tube sealed at the end and fitting closely inside the larger tube. Sufficient camphor was taken to give a column of pressed material about 15 mms. long.

The temperature of the paraffin was raised rapidly until the camphor melted to a clear liquid (about 180°), and allowed to fall until the camphor resolidified. Heating was applied gently, the camphor slowly remelted, and the melting-point of the camphor was taken as the temperature at which the last trace of crystalline material just disappeared. This was repeated until three consistent determinations were obtained.

A specimen-tube, specially cleaned with a mixture of sulphuric acid and chromic acid was weighed directly on an air-damped balance. 0.02 gm. of the product was added, and then 0.2 gm. of finely divided camphor, the weight being noted after each addition. The two substances were melted together to give a homogeneous solution by closing the tube with a cork to prevent loss of camphor by sublimation, and melting/

melting the camphor by direct heating. The molten material was swirled around in the tube to ensure good mixing, and then allowed to cool.

The mixture was then removed from the tube, and this was best done while the camphor was still warm, as otherwise the melt became very hard and the tube might have to be broken with the consequent risk of contamination by fragments of broken glass. The camphor was ground up in a mortar in order further to ensure a homogeneous mixture, and the melting point of this solution determined as above. The molecular depression constant for camphor was found using benzoic acid, and a value of 400 was obtained.

Several determinations of the molecular weight of the product purified from dioxan were carried out and gave the following results for varying concentrations of the solution of the substance in camphor.

| Concentration of Solution. | Molecular Weight. |
|---|---|
| 1 : 10 | 582 |
| | 605 |
| 1 : 8 | 760 |
| | 751 |
| 1 : 7.5 | 814 |
| | 795 |
| 1 : 7 | 642 |

With concentrations greater than 1 part of substance in 7.5 parts of camphor variable results were obtained, probably due to the insolubility of the product above that limit.

Taking an average value for these molecular weights as lying between 700 and 750°, this would give a molecular formula for the substance of twice the empirical formula, already/

already established by analyses, $2 \times C_{28}H_{26}O$, with a molecular weight of 2 x 378 = 756. Thus this compound would seem to have been formed by the elimination of water from 8 molecules of benzyl alcohol or from 4 molecules of the ether.

## III. REACTIVITY OF THE PURIFIED PRODUCT.

In an effort to arrive at its constitution, the degradation of the product from the action of dibenzyl ether and sulphuric acid was attempted both by oxidation and reduction methods. In these experiments difficulties were encountered due to the insoluble nature of the compound.

### (a) Oxidation.

Degradation by oxidation methods was first tried using the common oxidising reagents, such as chromic anhydride and potassium permanganate in sulphuric acid, but in every case the product was recovered unchanged. At first this was thought to be due to the insolubility of the compound in these oxidising mixtures, and so glacial acetic acid, in which the product is slightly soluble, was used, with chromic acid as the oxidising agent. For the same reason, potassium permanganate in acetone solution was tried, but even on boiling for a considerable time, neither of these mixtures attacked the compound. In this connection dioxan was not used as a solvent, on account of its tendency to peroxidise, and thus cause violent explosions.

Oxidation in a sealed tube was then attempted using temperatures up to 240°. The product remained very stable to all the above reagents under these conditions, and no compound other than the original material could be isolated after the reaction. Above 240°, charring of the product became excessive.

Nitric acid was also used as an oxidising agent, but the dilute acid had no action even on heating in a sealed tube while fuming nitric acid caused the formation of a nitro derivative, similar to that described later (see page 45)

A similar series of oxidation experiments were carried out using the nitro compound, prepared by the action of a mixture of equal volumes of concentrated nitric and sulphuric acids, but this derivative showed the same stability towards oxidising agents as the original substance.

(b) Reduction.

Since the product under examination was saturated, the milder methods of reduction were not considered. Tin and hydrochloric acid was the first reagent to be tried, but as was the case with the oxidation experiments, the product showed marked stability, presumably owing to its insoluble character. A Clemmensen reduction using amalgamated zinc and hydrochloric acid was carried out with no more success, and reduction by means of metallic sodium was found to be impossible owing to the insolubility of the product in alcohols in general. The use of dioxan as a solvent medium was tried, but the addition to this solution of an alcohol, even in small amounts, caused precipitation of the product.

Red phosphorus and hydriodic acid, heated with the product in a sealed tube was also used as a reducing agent. Reduction by this means usually takes place at 130-140° with the formation of phosphonium iodide, but at this range no reaction took place, while at higher temperatures the problem of charring arose, and no satisfactory results were obtained. On several occasions, after the sealed tube had been opened, an odour reminiscent of diphenylmethane was noticeable, but no product other than the/

the starting material could be separated from the reaction mixture.

The chief difficulty experienced with all the reduction experiments was the insoluble nature of the original substance, and the consequent difficulty of obtaining intimate contact with the reducing agent. In an attempt to overcome this, reductions were carried out by heating the product with zinc dust in a current of hydrogen. As the substance did not distil, the zinc dust had to be mixed directly with the powdered material, and the mixture heated in a combustion tube through which a stream of pure hydrogen was passing. In these experiments, temperatures up to 400$^{\circ}$ could be used without any charring taking place, but no new material was isolated from the mixture after heating, nor was any volatile constituent removed in the current of hydrogen gas.

This experiment is interesting in view of the fact that Wagner-Jauregg and Griesshaber have reported the isolation of small amounts of terphenyl by the dry distillation of the compound which they obtained from dibenzyl either by the action of phosphorus pentoxide in chloroform solution. (c.f. page 14).

### (c) Acetylation, etc.

In the determination of the structure of this compound, it was important to find out the nature of the linkage which bound the oxygen atom in the molecule. In addition to an ether linkage, the oxygen may be present in the form of a hydroxyl group, and in order to examine this possibility, the preparation of the usual derivatives of that group/

group was attempted.

Acetylation was first tried by heating the compound with a mixture of acetic anhydride and acetic acid, but as the action of undiluted anhydride was not sufficient, catalysts such as zinc chloride and fused sodium acetate were employed. A mixture of acetyl chloride and pyridine was also used as acetylating agent; the reaction product, however, was very sparingly soluble in these reagents and was returned unchanged in each case.

Several benzoylations were conducted by the Schotten-Baumann reaction, and after these experiments several purifications in dioxan solution were necessary before it could be definitely stated that the starting material had not been attacked.

The preparation of further derivatives, using p-nitrobenzoyl chloride and 3:5 - dinitrobenzoyl chloride was attempted, but in these reactions the difficulty of solubility was again encountered and the product was returned unchanged.

## IV. DERIVATIVES OF THE REACTION PRODUCT.

Two derivatives of the product from dibenzyl ether and sulphuric acid have been obtained, a nitro compound produced by direct nitration with a mixture of equal volumes of nitric and sulphuric acids, and a bromo compound prepared by the direct action of bromine in chloroform solution.

### (i) Nitro Compound.

The nitration was carried out in the cold, the nitrating agent being a mixture of equal volumes of concentrated nitric and sulphuric acids. To ensure efficient agitation, part of the sulphuric acid was added to the powdered product to form a slurry, which was mixed with a mechanical stirrer. The remainder of the sulphuric acid and the nitric acid were then added slowly to avoid any rise in temperature, and the mixture stirred for several hours. A large excess of the nitrating agent was used, but no external heat was applied. The nitro compound was separated from the mixture by pouring into water, and was purified after washing free from sulphuric acid, by precipitation from acetone solution with ethyl alcohol M.P. 186-188.

This nitro derivative has no crystalline structure, but separated as a yellow powder which on analysis gave N = 8.3% and 8.45%. These figures would suggest that the compound contained one nitro group for each $C_7$ unit, i.e. four nitro groups for the formula $C_{28}H_{26}O$.

This compound would have a nitrogen content of 9.1%.

The composition of the nitro compound was confirmed by the preparation of the amino compound by the reduction/

reduction of this derivative with tin and hydrochloric acid. Part of the hydrochloric acid was added to the mixture of the nitro compound and an equal weight of granulated tin in a round bottom flask with upright condenser and the remainder added at such a rate as to keep the liquid boiling quietly. After the acid had all been added, the reaction mixture was heated for an hour to dissolve the rest of the tin and complete the reduction.

The amine was precipitated from the acid solution by treatment with excess alkali, but it rapidly became dark in colour on exposure to the air. As a result, before the analysis of this compound was carried out, it was converted to the acetyl compound by boiling the reduction product after filtration and drying, with acetic anhydride. The acetyl compound was precipitated on pouring the reaction mixture into water, and was purified by treatment with "Norite" in dioxan solution from which it separated as a white powder. N = 7.5%, 7·7%. The corresponding derivative of the nitro compound already described would have the formula $C_{28}H_{22}O.(NH.COC\ H_3)4$ and the theoretical nitrogen content of this compound is 8.01%. When the nature of the product is considered, these experimental values, although rather low, are sufficiently accurate to confirm the number of nitro groups present in the nitro derivative. From these results, a hydrogen in each $C_7H_7$ unit would appear to be replaced by $NO_2$.

(ii) Bromo Compound.

This was made by the direct treatment of the compound with bromine. The action took place readily in the cold and it had to be controlled by the addition of chloroform/

chloroform.

5 gms. of the product were dissolved in 20 ml. chloroform and treated with an excess of bromine (3 gms.) in 20 ml. chloroform. After a short time there was rapid evolution of hydrobromic acid gas, and the solution was heated gently until this had ceased. The bromo derivative was obtained from the chloroform solution by precipitation with absolute alcohol, when it separated as a pale yellow powder.

The derivative was very difficult to combust and required prolonged heating in the presence of cobalt oxide for the determination of carbon and hydrogen

C = 53.1%  H = 3.5%
53.7%  3.41%

These results again indicate the substitution of one atom in each structural unit $C_7H_7$ since a derivative of this type would have the formula $C_{28}H_{22}O\ Br._4$ and an analysis of C = 55.2%, H = 4.2%

## PURIFICATION OF THE REACTION PRODUCT OF DIBENZYL ETHER AND 80% SULPHURIC ACID BY TREATMENT WITH ALUMINA.

Further purification of the product from the reaction of dibenzyl ether and sulphuric acid was carried out by a similar method to that described by Wagner-Jaeuregg and Griesshaber in their paper on the action of phosphorus pentoxide and dibenzyl ether. (see page 11). This consisted in the treatment of the product in benzene solution with alumina, and subsequent precipitation of the filtrate with petroleum ether. These authors do not give details as to how this treatment was carried out, and so it was presumed that it had been conducted by the method used in chromotographic adsorptions. These adsorptions have been applied with some success to the isolation of substances which cannot be separated by crystallisation. Advantage is taken of the fact that the constituents of the mixture, usually coloured, exhibit different affinities for adsorbents (alumina, silica gel, calcium carbonate, etc.) the solution of the mixture (usually an organic solvent is used) being drawn through a filter tube filled with the adsorbent. The zones in which the separate constituents are fixed, are demarcated by moving the unadsorbed material further down the column or by washing it away altogether with a solvent other than that initially employed. As a result of this "development" the zones are separated from each other mechanically and "eluted" with suitable solvents.

Frequently colourless substances can also be separated and purified by this procedure provided that the chromotogram, prepared in a tube of special glass or quartz, can be divided up in the light of a mercury vapour lamp/

lamp, in accordance with the fluorescence induced.

As the product under examination was almost colourless this latter method had to be used, and the reaction product for this purpose was prepared as previously described, taking the precautions which had been found necessary to obtain a satisfactory solid product. This substance, after drying under vacuum, was treated with dioxan and alcohol, and this solution was boiled several times with "Norite" to remove the yellowish tinge which was always present. After drying, the product was freed from the last traces of dioxan by heating in a vacuum oven at 60°, i.e. a few degrees below its initial softening point.

The adsorption was carried out in a quartz tube with a constriction at one end over which was placed a perforated porcelain disc, on which the column of adsorbent rested. The lower end of the tube was fitted into a pressure flask to which suction could be applied. The adsorbent was alumina, prepared by Merck, and the solvent was a mixture of benzene and petroleum ether.

The packing of the alumina column was found to be of considerable importance, as it was undesirable that cracking or channeling should occur. The first method used was to mix the alumina with benzene to form a slurry which was poured into the tube under slight suction. The benzene drained through, leaving a cake of alumina. It was difficult, however, to avoid cracking of this cake when most of the benzene had been filtered off, and in later experiments the alumina was added to the tube in the dry state in small amounts, and by tapping and gently pressing with a glass rod after each addition, a compact column was formed. Successive additions of the adsorbent were/

were made until a column 30 cms. long was obtained.

In the initial experiments, benzene was used as solvent, but it was found that several treatments with fresh alumina were necessary to remove completely the trace of yellow colouring matter which still remained after purification with "Norite". As a result the benzene solution was diluted with petroleum ether until the dissolved product was almost precipitated. This also prevented the possibility of the adsorbed material being washed out of the alumina during the development stage.

A solution of 3 gms. of the purified product in 200 gms. benzene was filtered slowly through the alumina column, care being taken that there should always be a small quantity of solution on top of the alumina, since it would crack if it were allowed to become dry.

When this tube was exposed to the light from an ultra-violet lamp it was seen that, whereas the greater part of the tube showed no fluorescence, a band near the outflow end fluoresced brightly. On subsequent examination, it was found that this band of fluorescence, coincided exactly with that portion of the tube which had been protected from the direct action of light by the rubber stopper of the pressure flask.

Continued exposure of the unprotected tube to the ultra-violet light caused that part of the tube which was opaque to assume a brownish tinge, while the fluorescent band in its turn gradually became opaque. Since it was thought that this change was due to the actinic action of the light, the whole experiment was repeated, taking care that the reaction product was exposed to the direct action of light on as few occasions as possible.

As the facilities for carrying out the whole reaction/

reaction in a dark room were not available, the reaction vessel containing the sulphuric acid mixture was covered with several layers of dark glazed paper which is impervious to light,and it was noticed on the completion of the reaction that the product obtained was lighter in colour than that which had previously been formed in an unprotected flask. The apparatus used during the purification was similarly protected, as was the quartz tube containing the alumina.

3 gms. of the purified product in 100 gms. benzene to which petroleum ether had been added until the solution was almost precipitated, was filtered through the specially prepared alumina column, and when the quartz tube containing the alumina was exposed in the light of the mercury vapour lamp, it fluoresced completely and showed no separation into zones. The benzene-petroleum ether solution which had passed through was now almost colourless. The distribution of the adsorbent material in the alumina was found by dividing the alumina column into three parts and extracting each part separately in a special soxhlet apparatus, in which the extraction takes place near the boiling point of the solvent.

In the majority of extractions of matter chromotographically adsorbed it would appear from the literature that the extraction of adsorbed material is done using an alcohol, but this was not possible in this case due to the low solubility of the substance in that solvent. As a result, chloroform was used in these extractions, and of the 1.1 gms. of substance obtained from the alumina, 1 g,. was in the portion taken from the top of the tube. The remaining 0.1 gm. was found in the centre fraction, while/

while no solid material could be obtained from the bottom layer even after prolonged extraction.

The volume of solvent required for "developing" the alumina was investigated by increasing the amounts used in successive experiments by 50 ccs. Using benzene alone, it was found that after 200 ml. had passed through, very little material could be obtained on extraction with chloroform, showing that the solubility of this liquid was too great for this purpose. The best distribution throughout the column was given with 200 ccs. of a 3:1 mixture of benzene and petroleum ether using an alumina column of 30 cms.

10 gms. of the purified product which had been protected from the action of light, was dissolved in 300 mls. benzene and petroleum ether added until the solution almost became cloudy. This solution was filtered slowly under suction through the quartz tube filled with alumina as previously described. After it had passed through once, the solution was still slightly yellowish in colour, so it was passed again through a fresh alumina to obtain a colourless liquid.

The quartz tube containing the alumina was "developed" with 200 ccs. of benzene-petroleum ether mixture and examined under the ultra-violet lamp. The whole tube fluoresced brightly, but no zones were observed in the alumina. Further developing with 100 ccs. of the mixture of benzene and petroleum ether was carried out, and since this did not show the formation of zones, the alumina in the tube was completely extracted with chloroform. The final extraction of the alumina was carried out using dioxan as solvent, and the solid obtained from these extractions was precipitated with petroleum, and/

and purified by treatment with "Norite" in benzene solution. Yield of solid extracted from the alumina = 3 gms.

The colourless benzene-petroleum ether solution which had passed through the alumina was evaporated off, leaving a white solid which had none of the yellowish brown colour of the original material. Yield = 6.5 gms.

The melting points of the original product and the two substances separated by the alumina treatment, were carefully examined, and it was found that the material which had passed in solution through the alumina, had a lower melting point than either the untreated product or the substance which had been extracted from the alumina by chloroform.

| | M.P. |
|---|---|
| Untreated Product.......... | 88-93 |
| Substance which passed through Alumina in Benzene-Petroleum ether solution... | 65-70 |
| Substance extracted from Alumina by Chloroform.............. | 90-95 |

Analyses of these two fractions separated by the alumina, were carried out and the following results were obtained.

1. Substance which had passed through Alumina in Benzene-Petroleum solution.

(a) Wt. of substance 0.0794 gms. $CO_2$ 0.2696 ∴ C = 92.6%
$H_2O$ 0.0497 H = 6.95%

(b) Wt. of substance 4.78 mg. $CO_2$ 16.104 C = 91.85%
$H_2O$ 3.01 H = 7.0%

11. Substance extracted from Alumina by Chloroform:

(a) Wt. of substance .0759 gm. $CO_2$ 0.2591 C = 93.09%
$H_2O$ 0.0471 H = 6.89%

(b) Wt. of Substance 3.904mg. $CO_2$ 13.31 C = 92.88%
$H_2O$ 2.49 H = 7.1%

From/

From these analyses it would appear that a hydrocarbon had been formed by this treatment with alumina, and this could take place by the removal of the elements of water from the compound with the empirical formula $C_{28}H_{26}O$, i.e. $C_{28}H_{26}O - H_2O = C_{28}H_{24} = 4 \times C_7H_6$.

A series of molecular weight determinations were carried out in camphor by the method already described (see page, 37), using varying concentrations of the substances in camphor. As was the case with the untreated product, these determinations gave different values for each concentration with a maximum value for a concentration of 1 part of substance to 8 parts of camphor. Above this limit, the results became erratic, due to the insolubility of the material in the camphor.

| Concentration. | (I) | (II) |
|---|---|---|
| 1 : 12 | 679 | |
| 1 : 10 | 723 | 842 |
| | 695 | 828 |
| 1 : 9 | | 905 |
| | | 922 |
| 1 : 8 | 904 | 837 |
| | 888 | 795 |
| | | 824 |
| | | 781 |
| 1 : 7 | 771 | 762 |
| | 815 | 774 |

These analyses and determinations of the molecular weight of the two products would seem to show that they are of a similar nature. Their carbon and hydrogen contents correspond closely to that of the hydrocarbon $(C_7H_6)x$, which has the following composition:- $C = 93.3\%$, $H = 6.7\%$. Taking an average value of the molecular/

molecular, weights in camphor as falling between 800 and 830, this would indicate that the compound consisted of nine molecules of the empirical structure, $C_7H_6$, and had a molecular weight of 9 x $C_7H_6$, i.e. 9 x 90 = 810.

The formation of this hydrocarbon from a product which, judging by the analytical results obtained for the carbon and hydrogen content by various independent investigators would appear to contain oxygen is a matter of considerable interest. The removal of the elements of water from this compound can be explained by the dehydrating effect of the alumina. Support is obtained for this theory from a reaction described by Sabatier and Mailhe (C.r.,1908, 147, 106), in which benzyl alcohol by the dehydrating action of metallic oxides, especially alumina, gave a yellow resinous substance to which these authors gave the formula $C_7H_6$. Thus the alumina treatment of the benzene solution of this product did not merely decolourise the solution, but had also brought about complete dehydration of the compound.

From these results, it would appear that the primary reaction of sulphuric acid on benzyl alcohol and debenzyl ether was the formation of a complex substance, which could be converted to a hydrocarbon by the removal of the elements of water on further treatment of the substance with alumina.

## REACTION OF SULPHURIC ACID WITH FURTHER ARALKYL ALCOHOLS.

I. p-Tolyl Carbinol.

II. p-Bromobenzyl Alcohol.

III. p-Nitrobenzyl Alcohol.

IV. m-Nitrobenzyl Alcohol.

## REACTION OF 80% SULPHURIC ACID WITH FURTHER ARALKYL ALCOHOLS.

Further investigation has been made into the reaction which takes place when aryl alcohols and ethers are treated with 80% sulphuric acid. Since it has been shown that the reactions of benzyl alcohol and dibenzyl ether with sulphuric acid gave the same product, in this series of experiments the alcohols have been used in preference to the corresponding ethers, because of their accessability. The alcohols used were substituted derivatives of benzyl alcohol, such as p-tolyl carbinol, and p-bromobenzyl alcohol. In order to ascertain whether the reaction with sulphuric acid takes place with nitrobenzyl alcohols and is not prevented by the presence of a nitro group, similar experiments were conducted with m- and p-nitrobenzyl alcohols.

The reactions were carried out by a similar method to that used with dibenzyl ether, and since the high-speed stirrer was used no difficulties were encountered due to reaction products separating out in the form of an oil.

I. <u>p-Tolyl Carbinol</u>. $CH_3C_6H_4CH_2OH$.

This alcohol was chosen first as an example of an alcohol in which the para-position to the alcoholic group was occupied. However, as the subsequent experiments proved, this methyl group did not prevent the reaction from taking place, whether by the elimination of water from the alcoholic hydroxyl and the hydrogen of the methyl group or a hydrogen atom attached to the nucleus, it was not possible to determine at this stage.

<u>Preparation of p-tolyl carbinol</u>.

This alcohol was made by the Cannizzaro reaction from p-tolualdehyde. 25 gms. of this aldehyde were shaken with 60% caustic potash in an atmosphere of nitrogen for an hour, and the resulting emulsion allowed to stand overnight. An inert atmosphere of nitrogen is necessary due to the ease of oxidation of the tolualdehyde, as otherwise a large proportion of toluic acid can be isolated from the reaction mixture. The caustic potash solution becomes almost solid on standing, and was diluted with water and extracted with ether. The ether extract was shaken with saturated sodium bisulphite solution to remove any unchanged aldehyde, washed with water, dried under anhydrous sodium sulphate, and the excess ether distilled off. Yield of Carbinol, 10 gms. M.P. 54-55°.

The aqueous liquor was acidified with hydrochloric acid to precipitate the toluic acid, which was also formed. Yield of acid = 14.5 gms.

The reaction was carried out in a small 100 ml. bolt-head, fitted with a thermometer and a high speed propellor stirrer as in the reaction with benzyl alcohol.

10/

10 gms. p-tolyl carbinol.
50 ml. sulphuric acid, S.G., 1.84.
21 ml. water.

The water and the sulphuric acid were mixed and heated to 140$^{\circ}$, and since the carbinol was a solid, it was added in powdered form. The reaction was exothermic and the addition of the tolyl carbinol took 5 minutes in order that the temperature should not rise beyond 140$^{\circ}$. Stirring was continued for a further 15 minutes at this temperature, the acid mixture poured into water, and the solid, which was precipitated, filtered off. This product could be separated into two fractions by extraction with ether. The fraction which did not dissolve in ether was purified by dissolving in dioxan and treating with norite.

(a) Yield of ether soluble fraction = 3 gms.
(b) Yield of fraction insoluble in ether = 6.5 gms.

(a) The ether soluble portion was purified by precipitation from ether several times, and then analysed by the hemi-macro method for the determination of carbon and hydrogen. White powder, M.P.78.These analyses gave the following results, C = 90.9%, 90.7%; H = 9.2%, 9.4%, and these values would seem to indicate the formation of a hydrocarbon. The simplest hydrocarbon nucleus which could be formed by the elimination of water from tolyl carbinol is $C_8H_8$, i.e. $CH_3C_6H_4.CH_2OH - H_2O = C_8H_8$ and a product with such an empirical formula would have the analysis C = 91.5% H = 8.5%.

Several determinations of the molecular weight of this hydrocarbon were made by the freezing-point method in benzene solution, and gave values varying between 820 and 840$^{\circ}$. Taking these values in conjunction with the carbon and hydrogen analyses, this hydrocarbon would have the molecular formula/

formula $(C_8H_8)_8$, i.e. a molecular weight of 8 x 104 = 832. Such a compound could be formed by the complete elimination of the elements of water from 8 molecules of p-tolyl carbinol.

(b) The other constituent was purified by treatment with norite in dioxan solution after repeated extractions with ether, and an analysis gave the following results. White powder. Melting range. 115-118°

| C | H | O (by difference) |
|---|---|---|
| 87.9 | 7.69 | 4.41 |
| 88.1 | 7.65 | 4.25 |

The product, analogous to that obtained from the reaction of dibenzyl ether and sulphuric acid, i.e. from 4 molecules of p-tolyl carbinol by the loss of three molecules of water, giving $C_{32}H_{34}O$, would have a percentage composition C = 88.5%, H = 7.85%, O = 3.65% and from these analysis it would appear that these compounds had been formed in a similar manner.

## II. p-Bromobenzyl Alcohol.

The reaction with sulphuric acid was also conducted using a halogen-substituted benzyl alcohol. The use of p.-bromobenzyl alcohol entirely excludes the possibility of reaction taking place in the para position to the alcoholic grouping. In spite of this, a reaction did take place, and the elimination of water by the sulphuric acid did not simply cause the formation of the corresponding di(p-bromobenzyl)ether.

Preparation of p-Bromobenzyl alcohol:- Jackson, Ber., 1878, 10, 1209.

This alcohol was prepared by the hydrolysis of p-bromobenzyl bromide through the acetate in a similar manner to p-nitrobenzyl alcohol.

p-Bromobenzyl bromide was best made by the direct bromination of bromo-toluene by boiling with the theoretical quantity of bromine in the sunlight. The mixture was heated until the evolution of hydrobromic acid had ceased, and on cooling, the product was recrystallised from alcohol.

Hydrolysis of this bromide took place by prolonged boiling in water, but it was best performed through the acetate which was prepared by heating the alcoholic solution with potassium acetate. This derivative was hydrolysed with alcoholic caustic potash and the alcohol was crystallised from benzene solution in needles. M.P. $75^{\circ}$.

It is of interest to note that, when attempting to prepare di(p-bromobenzyl)ether from bromobenzyl alcohol, Errera found that the use of sulphuric acid or boric anhydride did not give the desired ether, but a semi-solid product which was not identified. (Gazz., 18, 240).

The/

The reaction with sulphuric acid was conducted in the usual way, and the acid mixture was poured into water. The solid which separated was filtered and washed with water several times and dried under vacuum. This product was practically insoluble in alcohol and ether even on boiling, and after repeated extractions with ether a small amount of material was obtained which on recrystallisation from alcohol proved to be dibromobenzyl ether. M.P. 73-74°.

The bulk of the product was purified by treatment with Norite in dioxan solution from which it separated as a yellowish-brown powder. M.P. 175-178.

On analysis this fraction gave the following values for carbon and hydrogen :- C = 52.8, 52.5% H = 3.7, 3.68%. This compares with a percentage of carbon = 53.1% and hydrogen = 3.3%, for a product formed by the elimination of 3 molecules of water from 4 molecules of the bromobenzyl alcohol, as was the case with dibenzyl ether, i.e. 4 x Br. $C_6H_4CH_2OH - 3H_2O = Br_4C_{28}H_{22}O$.

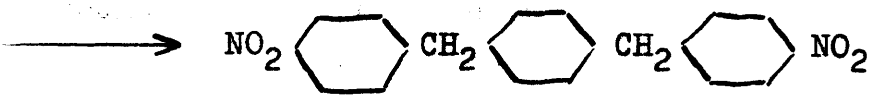
## III. p-NITROBENZYL ALCOHOL. $NO_2C_6H_4CH_2OH$

This alcohol was used in order to find out whether the reaction of aryl alcohols and sulphuric acid was inhibited by the presence of a nitro group in the para position to the alcoholic grouping, or took place in the normal manner.

p-Nitrobenzyl alcohol was made from the acetate obtained by boiling p-nitrobenzyl chloride with alcoholic potassium acetate solution (Basler, Ber., 1883, 16, 2713) 20 gms. of this acetate were dissolved in 40 mls. ethyl alcohol, the solution heated to 60°, and 35 mls. 15% caustic soda solution added. The hot mixture was shaken vigorously and cooled quickly after 5 minutes by pouring into ice-water. The aqueous liquer was extracted with ether and the alcohol recrystallised from that solvent. M.P. 93.

This alcohol condenses with benzene in the presence of concentrated sulphuric acid to give the nitro compound $C_{20}H_{16}N_2O_4$. The positions in the benzene nucleus from which the elements of water are eliminated are not given by Basler, but they are presumed to be "para" to one another.

$$NO_2C_6H_4CH_2OH + H\ C_6H_4H + HOH_2C\ C_6H_4NO_2$$



## EXPERIMENTAL.

10 gms. p-Nitrobenzyl Alcohol.
50 ml. sulphuric acid. S.G. 1.84
21 ml. water.

The reaction was carried out as in the previous experiment, but in this case the addition of the p-nitrobenzyl alcohol only required 2 minutes, as there was not the usual evolution of heat. The reaction mixture was maintained at 140° for a further 15 minutes, and poured into water. The solid which separated, was completely soluble in ether from which it could be recrystallised. M.P. 176-178°. Pale yellow needles. Yield = 9 gms.

Since it had been noticed during the experiment with sulphuric acid that the reaction with this alcohol was not so strongly exothermic as in the previous cases, the possibility that the reaction had not proceeded in the normal manner was not overlooked. The simple ether of p-nitrobenzyl alcohol, di(p-nitrobenzyl)ether is not reported in the literature but on analysis, the percentage composition of this compound was found to correspond closely with that required by such an ether.

| | C | H | N |
|---|---|---|---|
| Theory | 58.3 | 4.2 | 9.7 |
| Found | 58.1 | 4.60 | 9.85 |
| | 57.9 | 4.45 | 9.60 |

From these figures it will be seen that the reaction, analogous to that with benzyl alcohol had been inhibited by the presence of the nitro group in the para position to the alcoholic group, since the treatment of this alcohol with sulphuric acid had resulted in the formation of the corresponding ether, di(p-nitrobenzyl) ether.

## IV. m-NITROBENZYL ALCOHOL.

m-Nitrobenzyl alcohol was prepared from the corresponding aldehyde by the Cannizzaro reaction (Ber., 1882, 15, 2090). 25 gms. m-nitrobenzaldehyde were added to a solution of 10 gms. caustic potash, 10 mls. ethyl alcohol and 50 mls. water. The mixture was kept cool during the initial addition and after shaking vigorously, was allowed to stand overnight. The solution was extracted with ether, and when this was evaporated off the alcohol remained as a pale yellow oil. This liquid was distilled at 175-180° under 3 mms. pressure, but due to its low melting point (27°) the alcohol did not crystallise at room temperature. Like p-nitrobenzyl alcohol, this alcohol reacts with benzene in the presence of sulphuric acid to give a nitro compound.

10 gms. m-nitrobenzyl alcohol.
50 mls. sulphuric acid.
21 mls. water.

The reaction was performed by the standard method and as this alcohol was liquid, it was added to the hot acid mixture from a dropping funnel. The product was obtained by pouring the reaction mixture into water, and it was purified by dissolving in dioxan and precipitating with ethyl alcohol M.P. 142-145.

Analyses showed that the substance was analogous to that obtained from benzyl alcohol, i.e. the empirical formula corresponded with the composition of a compound formed by the elimination of three molecules of water from four molecules of m-nitrobenzyl alcohol:-

$$4 \times NO_2C_6H_4CH_2OH - 3H_2O = C_{28}H_{22}O_9N_4.$$

Analyses/

| | Analyses of Product. | Theoretical Values. |
|---|---|---|
| C% | 59.5 | 29.95 |
| | 59.41 | |
| H% | 4.25 | 3.95 |
| | 4.05 | |
| N% | 9.85 | 10.05 |
| | 9.97 | |

Thus, unlike the "para" nitrobenzyl alcohol, the elimination of the elements of water from this alcohol had not stopped at the stage of formation of the primary ether, di (m-nitrobenzyl) ether, but that a secondary reaction had taken place presumably through the hydrogen atom in the para position to the alcoholic grouping.

# Summary of the reactions of 80% Sulphuric Acid with certain aryl alcohols.

## SUMMARY OF THE REACTIONS OF 80% SULPHURIC ACID WITH ARALKYL ALCOHOLS.

The series of reactions which have been carried out with 80% sulphuric acid and substituted benzyl alcohols has shown that except in special cases the aralkyl alcohols react with sulphuric acid in a similar manner to benzyl alcohol. The reaction of this alcohol takes place readily to give a product to which the empirical formula $C_{28}H_{26}O$ has been assigned, and from molecular weight determinations it would appear that the compound exists in solution as the double molecule $C_{56}H_{52}O_2$.

Treatment of this product with alumina (see page 48) gives a hydrocarbon with the formula $(C_7H_6)_8$, and this elimination of water can best be explained by the dehydrating action of the alumina; i.e. $C_{56}H_{52}O_2 - 2H_2O = (C_7H_6)_8$.

Since the directing influence of the alcoholic group in the benzyl alcohol nucleus is ortho and para, the most probable course of reaction is the formation of a chain by elimination of water through the hydrogen atom in the para position, but at the same time occasional ortho and perhaps meta linkages may occur to render the chain unsymmetrical.

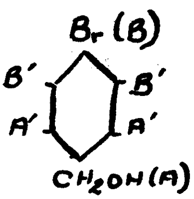
From an examination of the products obtained by the action of 80% sulphuric acid with these substituted benzyl alcohols, it can be stated that the elimination of water does not always take place through the hydrogen atom in the para position to the alcoholic group, but rather is it dependent on the nature of the substituent groups in the nucleus.

Varying results would appear to have been obtained with the three para-substituted alcohols which were used, but on closer examination it will be seen that these results are in/

in accord with the activating influence of the groups in the benzene ring. The alcoholic group in the nucleus directs ortho and para, and since the para position is occupied, those positions ortho to the alcoholic group, alone are affected by this group.

Only in the case of p-nitrobenzyl alcohol was para substitution sufficient to inhibit any further reaction than the formation of the simple ether, despite the meta-directing influence of the nitro group i.e. towards those positions ortho to the alcoholic group. These positions are already influenced by the alcoholic group, and the absence of reaction with this alcohol can best be explained by the well known fact that a nitro-group depresses the activity of these nuclear hydrogen atoms adjacent to it.

On the other hand, since the presence of a bromine atom in a nucleus does not adversely affect the activity of the hydrogen atoms in that nucleus it is not surprising that the reaction between p-bromobenzyl alcohol and sulphuric acid proceeded in the normal way. The activating influence of the bromine atom is ortho and para, and thus all four free hydrogen atons in the nucleus are activated, i.e. if the alcoholic group is represented by A. and the bromine atom by B, A' and B' indicate the positions activated by these groups. However, considering the relative activity of these substituent groups, it is most probable that the reaction takes place through the ortho position to the bromine atom, i.e. meta to the alcoholic group instead of para as in the case of the unsubstituted benzyl alcohol.



p-Tolyl carbinol is not analogous in constitution to the other para-substituted alcohols, with which the reaction with sulphuric acid was carried out, since the methyl/

methyl group in the para position might be reactive towards hydroxyl by the elimination of water. From the reaction of this alcohol with sulphuric acid, it was found that two products were obtained, the one formed in an analogous manner to the reaction product from benzyl alcohol and containing a small percentage of oxygen, the other a hydrocarbon the analysis of which showed that it had been formed by the complete elimination of water from 8 molecules of p-tolyl carbinol (See page 58).

From an examination of the structural formulae which may be postulated for this later compound, it will be seen that it is not possible to devise a scheme of synthesis for the formation of a saturated hydrocarbon which does not involve ring-closure in some part of the structure. This ring-closure may take place through the methyl group, although it must be remembered that in general the hydrogen atoms of a methyl group are not so reactive as the free hydrogen of the nucleus to which the group is attached. As in the case of p-bromobenzyl alcohol already discussed, the activating influence of the substituent methyl group in this alcohol is directed ortho and para, and it is most probable that reaction takes place chiefly through the positions ortho to the methyl group, although the possibility of reaction through the methyl group must not be overlooked.

The theory that the presence of a nitro-group in the nucleus of the alcohol would depress the reactivity of the nuclear hydrogen atoms, was examined by carrying out the reaction with m-nitrobenzyl alcohol. Unlike the case of p-nitrobenzyl alcohol, this reaction proceeded in the normal manner, and it can only be concluded from this result that the elimination of water took place through a hydrogen atom in/

in the ortho or para position to the alcoholic group. As has already been stated, the treatment of the product from the action of 80% sulphuric acid on benzyl alcohol or dibenzyl ether, with alumina, resulted in the formation of a hydrocarbon with the formula $(C_7H_6)_8$, and the production of such a compound has been explained by the elimination of water from the original compound $C_{56}H_{52}O_2$. Confirmation for this theory is obtained from the reaction of sulphuric acid with p-tolyl carbinol. In this case, two products were obtained, one containing oxygen and formed in a similar manner to the compound from benzyl alcohol, the other a hydrocarbon produced by the complete dehydration of this carbinol. The formation of these hydrocarbons requires that ring-closing of the molecule should take place, since no evidence of unsaturation in these compounds can be obtained, and such ring-closure may take place through the methyl group of p-tolyl carbinol as well as by means of a hydrogen atom attached to the benzene nucleus. It is interesting to note that only in the case of this alcohol, which contained a methyl group, was there direct formation of a hydrocarbon by the action of sulphuric acid.

Although it is not possible to draw a definite conclusion from these experiments, the results would seem to indicate that the reaction takes place by the elimination of water through the para hydrogen to the alcoholic group and that where this is prevented by the presence in the nucleus of an "inactive" substituent in the para position, the chances of reaction taking place are dependent on the nature of the substituent groups in the molecule.

No further evidence can be obtained from these reactions as to the structure of the compounds formed by sulphuric acid, and as the degradation of these substances into/

into simpler constituents both by oxidation and reduction methods, has proved to be very difficult, recourse had to be made to the method of synthesis in an attempt to obtain further information regarding the nature of these reactions.

# ATTEMPTED SYNTHESIS OF THE PRODUCT FORMED BY THE ACTION OF BENZYL ALCOHOL AND DIBENZYL ETHER WITH 80% SULPHURIC ACID.

When it was realised that the determination of the structure of the compound, obtained by the treatment of dibenzyl ether with 80% sulphuric acid, would prove difficult by degradation methods, methods of synthesis were attempted. All the evidence available both from the analysis of the compound, and from the composition of the products formed by the action of sulphuric acid with substituted benzyl alcohols, indicates that these compounds have a molecular formula which corresponds to that of the substance which would be formed by the removal of water from four molecules of the dibenzyl ether, or from eight molecules of the alcohol. The empirical formula which is given by these compounds is half of this molecular formula, and is equivalent to that of the substance which would be obtained by the removal of three molecules of water from four molecules of the simple alcohol; thus in the case of benzyl alcohol, this gives an empirical formula of $C_{28}H_{26}O$, i.e.

$$4 \times C_6H_5\ CH_2OH - 3\ H_2O = C_{28}H_{26}O..$$

This compound $C_{28}H_{26}O$ would have an analysis of Carbon = 89.4% and Hydrogen = 6.8%, and this corresponds closely to the mean values obtained for this compound by analysis, C = 89.6%, Hydrogen = 6.9%.

The molecular formula, which was established by taking a mean value of the molecular weights, found by Rast's method gives an actual molecular weight of 756. At the same time lower values for the molecular weight of this compound have been obtained using a concentration of one part of the substance to ten parts of camphor. Several determinations carried out both by the author and by Schoeller of Berlin, gave values for the molecular weight in the region of 600 (page 39) and from the variable results which/

which were obtained using different concentrations of camphor solution, it would appear that association of the molecules in solution had taken place; thus it is not unreasonable to suppose that the compound exists in the free state as $C_{28}H_{26}O$, and only forms the double molecule in the camphor solution. This formula $C_{28}H_{26}O$ would indicate a molecular weight of 378, but accurate determinations of the molecular weight with more dilute solutions giving values less than 582 were not possible, because of the small depression of the freezing-point.

A molecular weight of 582 is required by the compound which would be formed by the elimination of five molecules of water from six molecules of benzyl alcohol:-

$$6\ C_6H_5CH_2OH - 5\ H_2O = C_{42}H_{38}O$$

Such a compound would agree more closely with the minimum values of the molecular weight, but it would require a carbon percentage of 90.4, a figure which is higher by almost 1% than any value obtained during the series of analyses of the original product (see page 32).

The reaction by which benzyl alcohol and dibenzyl ether condense in the presence of sulphuric acid is similar to the formation of the condensation product from benzyl chloride (see page 14). This condensation product has been shown (Jacobsen, J.A.C.S.,1932,1513) to consist of chains containing the group - $C_6H_4CH_2$ - as the structural unit, with the coupling taking place mainly in the para position to the methylene group. By analogy with this structure, the following formula could be suggested for the compound $C_{28}H_{26}O$:-

$$C_6H_5CH_2C_6H_4CH_2.\ O.\ CH_2\ C_6H_4CH_2C_6H_5$$

This/

This type of condensation could take place readily with benzyl alcohol by the elimination of water between the alcoholic group and a p-Hydrogen from the nucleus of another molecule. This coupling may also contain occasional ortho and perhaps meta linkages which would render the chain unsymmetrical.

In order to produce such a compound from dibenzyl ether it is necessary to assume that this substance reacts as if it were split at the oxygen linkage by the sulphuric acid. This assumption is quite reasonable when it is remembered that dibenzyl ether is decomposed on heating to benzaldehyde and toluene, and it also accords with Hickinbottom's observation that the first stage in the migration of the benzyl group is the elimination of that group as the free radical (see page 26 ).

The synthesis of this product was attempted through the primary alcohol, p.-benzylbenzyl alcohol, since the suggested formula has a symmetrical structure and can be regarded as being formed by the condensation of two molecules of this alcohol:-

$$2.\ C_6H_5CH_2C_6H_4CH_2OH \longrightarrow C_{28}H_{26}O + H_2O$$

The only reference in the literature to a benzylbenzyl alcohol was made by Wertyporoch and Farnik (Annalen, 1930, 491, 271) in an investigation of the action of benzyl chloride and aluminium chloride in nitrobenzene solution. In addition to the usual condensation product $(C_7H_6)_x$, these authors isolated a small amount of material which they claim to have established by analysis to be chloromethyl diphenylmethane.

They also state that by the hydrolysis of this chloride in alcoholic solution with potassium acetate, and digestion/

digestion of the acetate formed, with caustic potash, they obtained from the residue an alcohol to which they ascribed the formula, $C_6H_5CH_2C_6H_4CH_2OH$, i.e. benzylbenzyl alcohol.

These authors described this alcohol as a pale yellow oil, boiling at $131^{\circ}$ under 0.13 mm., soluble in the usual organic solvents.

The yield in which this alcohol was obtained was very small and this method of preparation was unsuitable for the purpose of this research, since the positions in the benzene nuclei through which the coupling took place were not determined. No other references to the preparation of chloromethyl diphenylmethane are available, for unlike the corresponding ketone, the halogenation of phenyl p-tolylmethane cannot be controlled to give a specific compound. As a result, new methods for the preparation of p-benzylbenzyl alcohol had to be devised, and this synthesis comprises the next section of the work.

## SUMMARY OF SYNTHETIC METHODS USED IN ATTEMPTS TO PREPARE p-BENZYLBENZYL ALCOHOL.

Theoretically one of the simplest methods of preparing p-benzylbenzyl alcohol is through the Friedel and Crafts reaction by means of benzyl chloride and benzyl alcohol:-

I. $C_6H_5CH_2Cl + H.C_6H_4CH_2OH \rightarrow C_6H_5CH_2C_6H_4CH_2OH$

A method of synthesis closely resembling this can be formulated, using the Ullmann reaction. The reacting constituents in this case are benzyl bromide and p-bromobenzyl alcohol:-

$$C_6H_5CH_2Br + Br.\ C_6H_4CH_2OH \rightarrow C_6H_5CH_2C_6H_4CH_2OH.$$

The practical difficulty of the extreme reactivity of the benzyl halide was encountered in both experiments, and in addition the alcoholic group of benzyl alcohol had to be protected because of inter-molecular condensation in the presence of aluminium chloride.

II. Reduction of Diphenylmethane p-Carboxylic acid.

The acid analogue of p-benzylbenzyl alcohol, diphenylmethane p-carboxylic acid can readily be prepared and reduction of this acid was attempted in two ways, the first being the standard method of Bouveault and Blanc, by heating the ethyl ester of the acid with sodium in alcohol.

$$C_6H_5CH_2C_6H_4\ CooEt + H_2 \rightarrow C_6H_5CH_2C_6H_4CH_2OH + EtOH$$

The other reduction method was electrolytic and the nascent hydrogen was supplied by dissolving the acid in alcoholic sulphuric acid, and using this solution as the cathode electrolyte in an electrolytic cell. This reduction was/

This reduction was complicated by the esterification of the acid in the presence of sulphuric acid and although a product was obtained, the material was of such a complex nature that it could not be identified.

### III. Reduction ofp-Benzoylbenzyl alcohol.

Although the controlled bromination of phenyl p-tolyl methane is not possible, p-benzoylbenzyl bromide $C_6H_5CO\ C_6H_4CH_2Br$ can be prepared from the corresponding ketone by the direct substitution of bromine in the side-chain. From this bromide, p-benzoylbenzyl alcohol can be obtained by hydrolysis.

Various methods of reducing "ketonic" to"methylene" groups were used in order to carry out the reduction of this alcohol to p-benzylbenzyl alcohol.

$$C_6H_5CO.C_6H_4CH_2OH \longrightarrow C_6H_5CH_2C_6H_4CH_2OH$$

The Clemmensen reduction of this keto-alcohol using aqueous hydrochloric acid was incomplete, a large part of the alcohol being recovered unchanged, and when the reduction was carried out in absolute alcohol saturated with hydrochloric acid gas, the product was resinous in character.

Wolff's reaction, by which the reduction of a ketonic group is effected through the hydrazone or semicarbazone by heating with sodium in alcohol, was also considered, but it had to be abandoned because these derivatives have not been reported in the literature, neither was it possible to prepare them by any of the usual methods.

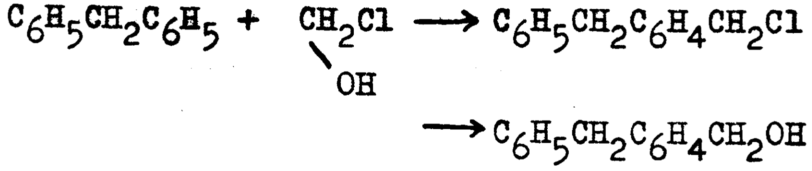
The most satisfactory means of reducing ketonic groups which are stable towards the normal reducing agents is by treatment with sodium in alcohol. Ethyl alcohol was first used as a solvent, but even at the boiling point the reduction was not sufficiently vigorous and most of the starting/

starting material was recovered unchanged.

The higher-boiling amyl alcohol was substituted for ethyl alcohol, and reduction took place at the boiling-point. From the product which was obtained, a fraction boiling at 143-145° under 4 mm. pressure was isolated. This distillate on analysis gave the following results, C = 86.3%, H = 9.1% as compared with C = 84.8% and H = 7.1%, the theoretical values for benzylbenzyl alcohol. After redistilling several times, it was found that the analysis of the product was not changed appreciably but since the values were approximately those of the desired alcohol, dehydration of the liquid to the compound, $C_{28}H_{26}O$, was attempted. Using the milder dehydrating agents, such as zinc chloride, no reaction took place, but with the more vigorous agents like sulphuric acid and phosphorus pentoxide, a solid product was immediately formed. This compound was very insoluble, and did not dissolve in dioxan and other common solvents; it was evidently not the desired product.

## IV. Blanc's Reaction.

Two other methods of synthesis of p-benzylbenzyl alcohol were devised using different starting materials. The first method made use of Blanc's reaction by which the group $CH_2Cl$ can be added to a hydrocarbon. The starting material in this case was diphenylmethane which it was desired to convert into p-benzylbenzyl chloride from which the alcohol can be obtained by hydrolysis.



$$C_6H_5CH_2C_6H_5 + \underset{\searrow OH}{CH_2Cl} \longrightarrow C_6H_5CH_2C_6H_4CH_2Cl$$

$$\longrightarrow C_6H_5CH_2C_6H_4CH_2OH$$

By/

By the action of formaldehyde and hydrochloric acid gas on diphenylmethane, an oily product containing a small amount of chlorine was obtained, but unlike the substance described by Wertyporoch and Farnik (Annalen, 1931, 491, 265) this oil did not distil under reduced pressure, and did not undergo hydrolysis when treated with alcoholic caustic potash.

## V. Stephen Reaction.

A scheme of synthesis for the preparation of benzylbenzyl alcohol through the corresponding alcohol can be devised by means of the Stephen reaction. By this method, phenyl p-tolyl nitrile would be converted to the aldehyde by the action of hydrochloric acid on an ethereal solution of stannous chloride and the nitrile. From this mixture the aldimine stannichloride complex of the nitrile should separate as a crystalline solid, and the aldehyde would then be obtained by hydrolysis with water.

$$C_6H_5CH_2C_6H_4CN \longrightarrow C_6H_5CH_2C_6H_4CHO.$$

It was found, however, that although this reaction worked well in the conversion of benzene to benzaldehyde, the more complex phenyl p-tolyl nitrile gave a very small yield of the aldimine stannichloride complex, which on decomposition with water gave only diphenylmethane p-carboxylic acid. Several experiments were carried out in which the conditions of hydrolysis of the tin complex were varied, and these reactions showed that when the temperature of the water was sufficiently high to bring about the decomposition of the aldimine compound, oxidation of the aldehyde took place, even in an inert atmosphere.

## Synthetic Methods used in the Preparation of p-Benzylbenzyl Alcohol.

I. Friedel and Crafts reaction.

II. Reduction of Diphenylmethane p-Carboxylic Acid.

III. Reduction of Benzoylbenzyl Alcohol.

IV. Blanc's Reaction.

V. Stephen's Reaction.

## I. SYNTHESIS OF p-BENZYLBENZYL ALCOHOL BY THE FRIEDEL AND CRAFTS REACTION.

Theoretically one of the simplest methods of preparing benzylbenzyl alcohol would appear to be by the Friedel and Crafts reaction from benzyl alcohol and benzyl chloride:-

$$C_6H_5CH_2Cl + H.C_2H_4CH_2OH \longrightarrow C_6H_5CH_2C_6H_4CH_2OH + HCl$$

However it has already been shown that benzyl chloride condenses readily to the insoluble hydrocarbon $(C_7H_6)_x$. Huston and Friedmann (J. Amer. Chem. Soc. 1916, 38, 2527) have reported that a similar reaction takes place with benzyl alcohol alone in the presence of aluminium chloride. During an investigation of the condensation of aromatic alcohols with Aromatic hydrocarbons, these authors mixed benzyl alcohol with a little more than the molecular equivalent of benzene and when the mixture was treated with anhydrous aluminium chloride, a vigorous exothermic reaction set in and hydrochloride acid gas was evolved. In addition to the diphenylmethane, which was isolated in 30% yield, they obtained a considerable amount of an insoluble hydrocarbon to which they assigned the formula $C_{27}H_{24}$. These authors indicated that this hydrocarbon would be more fully studied, but in their later work on this subject, it was merely referred to as a tar. (J. Amer. Chem. Soc., 1918, 40, 747).

Small scale experiments using benzyl alcohol and benzyl chloride were tried in the presence of aluminium chloride, but the reaction which took place was so vigorous even in the cold that it was recognised that the control of the condensation of these materials would be extremely difficult and further reactions by this method were not attempted.

Radziewanosk/

Radziewanoski (Ber., 1895, 28, 1138) recommends that in such reactions where difficulties are being met with, due to the polymerisation of benzyl chloride, the constituent other than the benzyl chloride should be present in large excess. In order to try this method of controlling the action it was first necessary to protect the alcoholic grouping of the benzyl alcohol, and this was done by direct methylation of the alcohol with methyl sulphate in caustic soda solution. (Dickhauser, Ber. 1911, 44, 2639).

Experiments were carried out using a large excess of benzyl methyl ether by dropping benzyl chloride slowly into a mixture of the ether and powdered aluminium chloride, cooled in ice. At this temperature there was no reaction but when heat was applied, hydrochloric acid gas was evolved, and the insoluble hydrocarbon $(C_7H_6)_x$ separated out. On pouring the mixture into water to destroy the aluminium chloride, it was found that the benzyl methyl ether could all be recovered unchanged.

Radziewanoski used aluminium amalgam in place of aluminium chloride for the condensation of benzyl chloride and benzene and this eliminated the formation of the insoluble hydrocarbon, provided the temperature was kept low. When this method was applied to the action of benzyl chloride and benzyl alcohol, no condensation took place in the cold, but polymerisation set in vigorously when the temperature reached 50°. Similar inactivity in the cold and polymerisation at higher temperatures was met with when benzyl methyl ether was used in place of the unprotected alcohol.

The preparation of a more active form of aluminium amalgam than that used by Radziewanoski, is described by Thiele and Merke, and when this was used, the conditions of reaction were similar to those with aluminium chloride.

Condensation/

Condensation of benzyl chloride took place even in the cold, while the benzyl methyl ether was recovered unchanged.

Meyer (J. Pr. Chem. 82, 538) has shown that benzyl ethyl ether reacts with benzene in the presence of phosphorus pentoxide to give diphenylmethane. On the other hand when benzyl ethyl ether was treated with benzene in the presence of aluminium chloride, little reaction took place but fractions of o- and p-dibenzyl benzene were isolated together with the hydrocarbon $C_{27}H_{24}$ (Huston and Friedmann, 1916, 38, 2528). The formation of an amorphous compound $(C_7H_6)_x$ from benzyl ethyl ether by the action of stannic chloride and thionyl chloride has already been described (See page 11).

From these reactions it would appear that benzyl ethyl ether showed a greater tendency to form polymeric hydrocarbons than the methyl ether and for this reason condensations involving its use were not attempted by the Friedel and Crafts reaction. In consequence the preparation of p-benzylbenzyl alcohol by this method was discontinued.

## EXPERIMENTAL.

Since it has been shown by Huston and Friedmann (see page 79) that benzyl alcohol reacts in the presence of aluminium chloride, the direct condensation of benzyl chloride and benzyl alcohol by the Friedel and Crafts reaction was not attempted. The alcoholic group was first protected by methylation to give benzyl methyl ether, and this compound was prepared by the following method of Dickhauser (Ber., 1911, 44, 2639).

100 gms. Benzyl alcohol.
100 mls. 10N Caustic soda.
100 mls. dimethyl sulphate.

The dimethyl sulphate was added slowly to the mixture of the caustic soda and the benzyl alcohol with constant agitation, at such a rate that the temperature did not rise above 40$^{o}$. When the addition was complete, stirring was continued for an hour, the liquid poured into water and distilled in steam. The distillate was extracted with ether and the excess ether removed in a water-bath, leaving a residue of benzyl methyl ether and unchanged benzyl alcohol.

Separation of these two constituents could not be carried out effectively by frational distillation, and the benzyl methyl ether was isolated by the following method devised by the author (W.G.C.), using ferrocyanic acid. This acid was prepared by mixing 20 gms. potassium ferrocyanide, 100 mls. water and 100 gms. 20% hydrochloric acid. The solution of ferrocyanic acid was added to the mixture of benzyl methyl ether and unchanged alcohol and shaken vigorously for five minutes until a crystalline complex salt of benzyl methyl ether separated out. This was filtered off, washed with ether to remove the last traces/

traces of benzyl alcohol, and the complex destroyed by treatment with dilute alkali. The benzyl methyl ether was recovered by extraction with ether, and purified by distillation. B.P. 170-171°.

Yield of pure benzyl methyl ether = 78 gms.
Theoretical Yield = 110 gms.
%age Yield = 71.

A series of Friedel and Crafts reactions were carried out using this ether in large excess over the theoretical amount required for reaction with benzyl chloride.

50 gms. Benzyl methyl ether (3 mols.)
15 ml. benzyl chloride (1 mol.)
5 gms. Aluminium chloride.

No carbon disulphide was used in these reactions as this solvent only caused condensation of the benzyl chloride to take place more vigorously. The powdered aluminium chloride was covered with benzyl methyl ether and the benzyl chloride added slowly, the mixture being kept cooled in ice. When the addition of the chloride was complete, the temperature was maintained at 0° for some time but there was only slight evolution of hydrochloric acid gas. The temperature was allowed to rise slowly to 20°, but still there was no indication of reaction; when, however, external heating was applied there was evolution of gas, with a rapid rise in temperature which had to be controlled by ice-cooling.

The reaction mixture was allowed to stand overnight and when it was poured into water, an insoluble solid was precipitated. This was filtered off, and the remaining liquid was extracted with ether and distilled. Most/

Most of the benzyl methyl ether was recovered by this means, leaving a small amount of an oily residue which did not solidify, and which was decomposed when further distillation was tried. 14 gms. of the insoluble hydrocarbon were obtained, and this showed that the benzyl chloride had been almost completely condensed in the presence of aluminium chloride.

Aluminium amalgam was used in place of aluminium chloride in order to prevent the excessive formation of the hydrocarbon polymer by the benzyl chloride. This was prepared by the method described by Radziewanoski. Aluminium foil was allowed to stand for some time in a solution of mercuric chloride, and then washed successively with water, alcohol and ether.

Condensation of benzyl chloride and benzyl alcohol was tried using the following quantities:-

20 gms. Benzyl Alcohol.
5 gms. Benzyl chloride.
5 gms. Aluminium amalgam.

With this mixture, no reaction took place in the cold, but when the temperature reached 80°, evolution of hydrochloric acid gas began. The reaction mixture was treated in the usual way, and it was found that most of the benzyl alcohol was recovered, leaving a residue of the condensation product formed by the benzyl chloride. Similar results were obtained by the use of benzyl methyl ether; no action took place in the cold, but decomposition of the benzyl chloride set in when the mixture was heated, leaving the benzyl methyl ether unattacked.

The preparation of a more active form of aluminium amalgam was described by Thiele and Merk (Annalen, 1916,415,265). Aluminium foil was cleaned by washing with caustic soda until strong/

strong effervescence of hydrogen took place, and then washed twice with water. The foil was then left to stand for 1-2 minutes in ½% solution of mercuric chloride, the foil washed with water and the operation repeated several times. The amalgam was dried with alcohol and ether and protected by covering with petroleum ether. When amalgam prepared by this method was mixed with a small quantity of boiling water, it reacted with evolution of hydrogen.

Weitz and Konig (Ber., 1924, 57, 167) state that the reactivity of the amalgam is further increased by using specially pure aluminium, that the foil should not be allowed to remain the mercuric salt solution for more than 15 seconds at a time but that this process should be repeated at intervals of a minute for half an hour.

Several experiments were carried out using the more active forms of aluminium amalgam. The product obtained by the method of Thiele and Werk, did not react in the cold but vigorous evolution of hydrochloric acid gas took place above $50^{\circ}$. Using the precautions recommended by Weitz and Konig, the aluminium amalgam was so reactive that reaction took place at ordinary temperatures although not with the same vigour as with aluminium chloride. In both cases, however, the products obtained showed that only inter-molecular condensation of the benzyl chloride had taken place and the benzyl methyl ether was recovered unchanged.

## II. REDUCTION OF DIPHENYLMETHANE p-CARBOXYLIC ACID.

(1) Preparation of Acid.

(2) Electrolytic Reduction.

(3) Bouveault and Blanc's Reaction.

## (1) PREPARATION OF DIPHENYLMETHANE p-CARBOXYLIC ACID.

Diphenylmethane p-carboxylic acid, the starting material in this synthesis of benzylbenzyl alcohol was made from p-tolunitrile according to the following scheme:-

(a) By chlorination in the side chain p-tolunitrile was converted to p-cyanobenzyl chloride. (Mellinghoff, Ber., 1889, 22, 3208)

$$CH_3C_6H_4CN + Cl_2 \longrightarrow Cl.CH_2C_6H_4CN + HCl$$

(b) Phenyl p-tolyl nitrile was obtained from p-cyanobenzyl chloride and benzene by the Friedel and Crafts reaction (Moses, Ber., 1900, 33, 2627).

$$C_6H_6 + Cl.CH_2C_6H_4CN \longrightarrow C_6H_5CH_2C_6H_4CN$$

(c) Hydrolysis of this nitrile yeilds diphenylmethane p-carboxylic acid.

$$C_6H_5CH_2C_6H_4CN \longrightarrow C_6H_5CH_2C_6H_4COO\ H$$

Phenyl p-tolyl nitrile was also used in the Stephen reaction for the preparation of p-benzylbenzyl alcohol through the corresponding aldehyde (see page 136)

## p. Tolunitrile. $CH_3C_6H_4CN$

This compound was prepared by the method described in the organic Syntheses (Coll., page 500), with a few modifications, according to the following practical details:-

625 gms. Copper Sulphate
162 gms. Sodium chloride
2 litres hot water

133 gms. Sodium Bisulphite
88 gms. Caustic soda in 1 litre of water

420 gms. Potassium Cyanide.

214 gms. p-Toluidine
500 ml. Hydrochloric acid

140 gms. sodium nitrite
400 gms. Water

500 ml. Benzene.

Cuprous chloride was prepared by dissolving the copper sulphate and sodium chloride in hot water in a large flask, fitted with a mechanical stirrer, and slowly adding the alkaline solution of sodium sulphite. The mixture was allowed to settle, after cooling to room temperature, and washed by decantation.

This cuprous chloride was suspended in a litre of cold water in a large basin fitted with a stirrer. The solution of the potassium cyanide in water was added and the mixture stirred when the cuprous chloride went into solution with considerable evolution of heat.

While the cuprous cyanide solution was cooling, the/

the p. toluidine was mixed with the hydrochloric acid and sufficient crushed ice added to keep the temperature below 0°. A solution of the sodium nitrite in water was added with stirring to the resultant suspension of toluidine hydrochloride, the temperature being kept between 0° and 5° by ice-cooling. The addition of the nitrite occupied about 5 minutes and the mixture gave free nitrous acid with starch iodide paper. The mixture was then neutralised with solid sodium carbonate, using litmus to give the end-point.

The cold cuprous cyanide solution was then cooled in ice to 0°, and 500 ml. benzene poured on the surface. To this was slowly added the cold neutralised solution of the diazonium compound. During the addition vigorous stirring was maintained and the temperature was kept at 0-5°.

As soon as the diazonium compound came into contact with the cuprous cyanide, a dark yellow oil was formed which soon gave off nitrogen. The resulting nitrile was taken up by the benzene immediately it was formed. When all the diazonium solution had been added, the temperature was held at 0° for half-an-hour, and then allowed to rise to that of the room.

When room temperature was reached, stirring was continued for one hour longer, and then the mixture warmed to 50° with steam to complete the decomposition of the diazonium compound. On standing two layers separated out, and the aqueous fraction was drawn off by syphon. The upper oily layer was distilled in steam until no more benzene and nitrile separated in the distillate. The water was separated off, and when all the benzene had been removed by distillation p-tolunitrile was collected at 104/106 under 20 mm.

Yield = 92 gms.

(a) p. Cyanobenzyl chloride. $CN.C_6H_4CH_2Cl$.

Chlorination of p. tolunitrile was carried out in several batches of approximately 25 gms. This was found to be preferable to chlorination in large quantities, since it reduced the loss due to the formation of higher chlorides after prolonged passage of the chlorine gas.

Chlorine gas, prepared by the addition of concentrated hydrochloric acid to potassium permanganate and dried by passing through sulphuric acid, was led into a retort containing the tolunitrile and bubbled through the hot liquid at a temperature of 140° until there was increase of weight of 30% due to the substitution of chlorine. Weight of Tolunitrile 25 gms.
Increase in Weight due to Chlorine 7.5 gms.

The passage of chlorine to give the required increase in weight occupied about four hours.

When the desired increase in weight had been obtained the liquid product was cooled in ice, and crystals separated out. After a short time the mass became almost solid and the oil remaining was filtered off. The crystals were dissolved in alcohol, treated with norite, and when the solution was cooled, white needles separated. M.P. 77-78°. Yield 21 gms.
The yield in this chlorination is greatly influenced by the purity of the tolunitrile, as the presence of a little impurity will adversely affect the crystallisation of the crude product from the chlorinated liquid on cooling with ice. It is preferable that the stream of gas should be fairly rapid, and that the passage of gas should be stopped shortly before the desired increase in weight/

weight has been attained, rather than run the risk of over-chlorination.

(b) Phenyl p. Tolyl nitrile.

21 gms. Cyanobenzyl Chloride.
30 gms. Aluminium chloride.
150 ml. Benzene (Dried over sodium).

The Aluminium chloride was powdered and covered with carbon disulphide in a 500 ml. bolt-head flask, fitted with a stirrer, to which was attached a mercury seal, and a reflux condenser. The cyanobenzyl chloride was dissolved in the dry benzene and added slowly to the mixture of carbon disulphide and aluminium chloride through a dropping funnel fitted on the end of the condenser. This addition took about 1½ hours and during the process hydrochloric acid gas was evolved even in the cold. The reaction mixture was allowed to stand overnight and then heated for four hours on a water-bath at 50° with constant agitation. On pouring the liquid on to ice, the oil which separated after the aluminium hydroxide had been dissolved by the addition of dilute hydrochloric acid, was extracted with ether, and the ether extract dried over anhydrous sodium sulphate. The ether, carbon disulphide and the bulk of the excess benzene were distilled off until the temperature reached 85°, and the residue was dissolved in alcohol and boiled for some time with charcoal. On cooling, an oil separated which owing to the low melting point of the nitrile (50°), was difficult to crystallise and required several purifications with Norite before colourless needles were deposited M.P. 48-49° Yield 20 gms.

(c) Diphenylmethane p. Carboxylic Acid.

Hydrolysis of phenyl p. tolyl nitrile is best carried out/

out by boiling the nitrile with alcoholic caustic potash under reflux for a short time.

20 gms. Phenyl p. tolyl nitrile.
100 ml. 30% Alcoholic caustic potash.

On boiling the solution for an hour, the acid was obtained by treating the alcoholic mixture with glacial acetic acid until all the caustic potash had been neutralised. After filtration the acid was purified by crystallisation from alcohol. MP.P. 157-158°
Yield - theoretical. 21 gms.

## (2) ELECTROLYTIC REDUCTION OF DIPHENYLMETHANE p. CARBOXYLIC ACID.

The electrolytic reduction of a carboxylic acid to the corresponding alcohol was first investigated by Mettler (Ber., 1905, 38, 1747) who found that the reduction of benzoic acid to benzyl alcohol could be successfully carried out in an electrolytic cell. Mettler found that 30% sulphuric acid gave the best yields and explained this result by the decreased solubility of benzoic acid in higher concentrations of acid. It is doubtful, however, if the use of more concentrated acid would have been practical, for it is probable that the stronger sulphuric acid would have reacted with the benzyl alcohol as soon as it was formed, in the same manner as in the reaction which is at present being investigated.

Mettler overcame the problem of solubility by using as the cathode electrolyte, a mixture of ethyl alcohol and sulphuric acid, containing 20-30% of sulphuric acid. The alcohol dissolved the benzoic acid readily, and this dilution of sulphuric acid enabled the desired electrolytic reduction to take place while preventing the condensation of the benzyl alcohol by dehydration. With this electrolyte it was necessary to keep the temperature of reduction as low as possible in order to prevent esterification of the aromatic acid with the ehtyl alcohol.

The importance of avoiding the esterification of the acid to be reduced is emphasised by the fact that reduction of the ester takes place under the same conditions as the acid, e.g. ethyl benzoate is reduced to ethyl benzyl ether.

$$C_6H_5COOC_2H_5 + H_2 \longrightarrow C_6H_5CH_2O\ C_2H_5$$

Esterification/

Esterification can be reduced by diluting the ethyl alcohol with water, while still maintaining the same concentration of acid. The cathode electrolyte now consisted of a mixture of 30% sulphuric acid, 35% ethyl alcohol and 35% water, and this alteration caused an increase in the working temperature of the cell from 25° in the case of the electrolyte containing 70% ethyl alcohol to between 55° and 60°. Under these conditions, benzoic acid was reduced to benzyl alcohol in 80% yield.

More recently Decans and Dufour (Bull. Soc. Chim. 1925, 37, 1167) have also been investigating the electrolytic reduction of benzoic acid and they conclude that the success of Mettler's method of reduction lies in the use made of the greater solubility of benzoic acid in warm dilute acid than in cold concentrated acid, while at the same realising the disadvantage of using ethyl alcohol as a solvent because of its tendency to cause esterification of the aromatic acid. With this defect in mind they have devised an apparatus in which the electrolytic reduction of benzoic acid can be carried out in 90% yield, using an electrolyte of boiling 30% aqueous sulphuric acid, containing no ethyl alcohol.

This method is interesting since it shows that the dehydration of benzyl alcohol by sulphuric acid is dependant rather on the strength of the acid than on the temperature of the mixture, for the boiling point of 30% sulphuric acid is approximately 100°, which is only 40° degrees lower than the temperature at which the dehydration experiments were carried out.

Ducans and Dufour found that the best results were obtained using electrodes of pure electrolytic lead, since the presence of any impurities considerably reduces the yield.

Baur/

Baur and Muller (Z. Electrochem angew. physik Chem., 1928, 34, 98; Chem. Abs., 1928, 22, 1894) report the electrolytic reduction of benzoic acid to 1:3 dihydro-benzoic acid. This result was investigated by Fichter and Stein (Helv. Chim. Acta, 12, 821), and they obtained an 80% yield of benzyl alcohol with only traces of hydroaromatic compounds by reductions in ethyl alcohol and sulphuric acid, using a pure lead cathode and a current density of 0.1 amperes per square centimetre. They conclude that the nuclear reduction observed by Baur and Muller was caused by the lower current-density which they used, 0.01 amp. per sq. centimetre.

By means of this method, it should be possible to prepare p. benzylbenzyl alcohol by the reduction of diphenylmethane p. carboxylic acid using 30% sulphuric acid and a current density of 0.1 amp./sq. cm.

$$C_6H_5CH_2C_6H_4COOH + H_2 \longrightarrow C_6H_5CH_2C_6H_4CH_2OH$$

Using a cathode electrolyte containing 70% ethyl alcohol, it was found that the working temperature of the cell was too low, and most of the diphenylmethane p. carboxylic acid was recovered unchanged. Dilution of the ethyl alcohol with water increased the reaction temperature, but esterification of the carboxylic acid took place. Conditions were finally established under which very little of the acid was recovered, but the product which was formed could neither be crystallised nor distilled, and its nature could not be determined.

An examination of the solubility of diphenylmethane p. carboxylic acid showed that it only dissolved slightly in 30% aqueous sulphuric acid, and it was probable that this would reduce/

reduce the chances of reduction by the method of Decans and Dufour. This was confirmed in an experiment in which all the carboxylic acid was recovered unchanged and under these circumstances the method was not investigated further.

## EXPERIMENTAL.

The electrolytic cell consisted of a tall 600 c.c. beaker, containing a porous pot (250 x 80 mm.) The anode in the beaker was a large sheet of lead bent to the curvature of the pot about 1 cm. from it and extending half way round the beaker. The cathode in the pot was a flag of pure electrolytic lead, which had been repeatedly amalgamated with mercury. The electrolytic lead was free from tin, since the presence of this impurity has a marked effect on the efficiency of reduction. The cathode measured 80 x 50 mms. giving a surface area of 40 sq. cms., and thus requiring a current of 4 amps. to give the desired current density of 0.1 amps/sq.cm.

Using this apparatus it was found that benzoic acid could be reduced to benzyl alcohol in 70% yield with a reduction time of 12 hours. Under similar conditions, Mettler found that 80 ampere hours were necessary, i.e. 20 hours at 4 amps., and the decrease in the time required can only be explained by the extreme purity of the lead used.

In the preliminary experiments which were carried out using diphenylmethane p. carboxylic acid, it was thought that esterification of the acid with ethyl alcohol in the cathode electrolyte was taking place but since this ester has not been characterised in the literature it was first prepared before any further experimental work was attempted.

## PREPARATION OF THE ETHYL ESTER OF DIPHENYLMETHANE CARBOXYLIC ACID.

Diphenylmethane p. carboxylic acid was prepared from p. tolunitrile by the method already described and esterification was carried out by boiling an alcoholic solution of the acid, containing 3% hydrochloric acid gas as catalyst, under reflux for 2 hours.

25 gms. Diphenylmethane p. Carboxylic acid.
100 ml. ethyl alcohol.

Hydrochloric acid gas was passed into a tared flask containing the ethyl alcohol until the increase in weight due to the gas was 2.5 gms. The recrystallised acid was then added to the flask and the mixture heated under reflux, but complete solution of the acid did not take place for an hour by which time the strong smell of ester was noticeable. Heating was continued for another hour to complete the reaction, and the hydrochloric acid remaining was removed by washing with water.

The oily precipitate of the ester was extracted with ether, and dried. Fractionation yielded a constant boiling liquid which was collected at 180° under 5 mm. pressure. Yield of Ester = 17 gms.

| | C | H. |
|---|---|---|
| Theory for $C_6H_5CH_2C_6H_4COOEt$. | 80.0 | 6.6 |
| Found | 79.8 | 7.1 |
| | 79.5 | 6.8 |

Hydrolysis of this liquid with alcoholic caustic potash, and subsequent treatment with glacial acetic acid, gave a white crystalline solid, M.P. 157-158°, which was shown to be diphenylmethane p. carboxylic acid.

## EXPERIMENT I.

Owing to the low solubility of diphenylmethane carboxylic acid in alcohol, the volume of the cathode electrolyte was doubled,using the same concentrations of alcohol and sulphuric acid as were used by Mettler in the reduction of benzoic acid.

| | | |
|---|---|---|
| Cathode | 15 gms. Diphenylmethane carboxylic acid<br>60 gms. sulphuric acid.<br>140 gms. ethyl alcohol | Anode.<br>30% Sulphuric Acid. |

This involved the use of an electrode of twice the surface area, i.e. 80 sq. cms., and as a result the time of reduction was decreased by one half, the current density being maintained at 0.1 amp./sq.cm.

The cell was switched on using a current of 8 amps. and when the cathode electrolyte had reached its working temperature of 30°, the carboxylic acid was added slowly, the speed of addition being governed by the rate of solution. After all the acid had been added, the current was allowed to run for a further ten hours. The cathode electrolyte was then poured into water, the liquid extracted with ether, and the ether extract dried with anhydrous sodium sulphate. When the ether was distilled off, it was found that the residue consisted of unchanged acid. Weight of residue = 14 gms.

## EXPERIMENT II.

Since the electrolytic reduction did not take place at 30°, the composition of the cathode electrolyte was altered in order to increase the reaction temperature. The dilution of the ethyl alcohol by half its weight of water gave an electrolyte with a running temperature of 65°. The cathode electrolyte now had the following composition:-

60 gms. Sulphuric acid.
70 gms. Ethyl Alcohol.
70 gms. Water.

The presence of the water reduced the solubility of the acid in the electrolyte, but this was offset by the higher temperature of reduction.

Using this electrolyte, the previous experiment was repeated without altering any of the other conditions. Most of the acid, however, was recovered unchanged, but in addition 1.5 gms. of an oil was obtained, boiling at 175-180 under 5 mm. This would seem to indicate that esterification of the carboxylic acid had taken place and this was confirmed by hydrolysis of the oil with alcoholic caustic potash. On treatment of this solution with glacial acetic acid, white crystals of diphenylmethane p. carboxylic acid were obtained. M.P. 156-157°.

EXPERIMENT III.

In an attempt to bring about reduction by this method, the time of the reaction was increased from 10 hours to 15 hours, i.e. 120 ampere hours. When the reaction mixture was poured into water, only a trace of diphenylmethane carboxylic acid could be recovered. From 15 gms. of the acid, 12 gms. of an oil were obtained which was soluble in alcohol and ether, but which could not be made to separate in a crystalline state from either of these solvents. The fact that this oil did not simply consist of the ethyl ester of the carboxylic acid was shown when distillation was attempted. Fractionation appeared to be beginning at 150° under 5 mm., but after a few minutes heating at this temperature, the liquid became dark in colour, and soon was completely charred.

## EXPERIMENT IV.

Further electrolytic experiments were carried out in which the temperature was increased to 80°, and the time of reaction to 20 hours. The increase of temperature was achieved, not by altering the composition of the cathode electrolyte but by external heating since it was found that dilution of the electrolyte increased the practical difficulties, due to the lower solubility of the carboxylic acid. Evaporation of the electrolyte took place gradually and the level of the liquid in the cathode pot had to be maintained by the addition of a mixture of alcohol and water, so as to keep the correct current density.

During the course of the reaction, the smell of ester was noticeable in the cathode electrolyte. When the reaction mixture was examined, no unchanged acid was recovered, and an ether extract contained a yellowish oil, such as was obtained in the previous experiment.

This oil could neither be distilled nor hydrolysed with alcoholic caustic potash and the ethyl ester of the carboxylic acid could not be separated from it. These results would seem to indicate that reduction had taken place, but in this connection, the conversion of ethyl benzoate to ethyl benzyl ether by electrolytic reduction (Ber., 1904, 37, 3190) must be borne in mind. It is possible that a similar reaction could take place with the ethyl ester of diphenylmethane p. carboxylic acid, which was shown in experiment II. to be one of the first products of reaction.

$$C_6H_5CH_2C_6H_4COOC_2H_5 \xrightarrow{H_2} C_6H_5CH_2C_6H_4CH_2OC_2H_5$$

Also/

Also, the possibility that the reduction of diphenylmethane carboxylic acid to benzylbenzyl alcohol had taken place, must not be overlooked. The esterification of these more complex acids and alcohols takes place readily and benzylbenzyl alcohol, as soon as it was formed, would be free to react with the unchanged diphenylmethane carboxylic acid. This complex ester in its turn is capable of undergoing reduction by the nascent hydrogen of the reaction mixture. In the event of such a series of reactions taking place, a product of the required structure would be formed according to the following scheme:-

$$C_6H_5CH_2C_6H_4COOH\ (I) \xrightarrow{H_2} C_6H_5CH_2C_6H_4CH_2OH\ \ (II)$$

$$\text{I. \& II.} \xrightarrow{\text{Esterification}} C_6H_5CH_2C_6H_4COOCH_2C_6H_4CH_2C_6H_5$$

$$\xrightarrow[\text{Reduction.}]{\text{Electrolytic}} C_6H_5CH_2C_6H_4CH_2OCH_2C_6H_4CH_2C_6H_5$$

In spite of several repetitions of this reduction, the liquid product which was obtained, could neither be distilled nor crystallised, nor could any separation be obtained by extraction with a series of solvents. Under these circumstances, no analyses were attempted, and the identity of the reduction product was not established.

## (3) ATTEMPTED REDUCTION OF p. BENZYLBENZOIC ACID BY BOUVEAULT AND BLANC'S REACTION.

The reduction of an acid to the corresponding alcohol has been successfully carried out by the method of Bouveault and Blanc. (Compt. rend., 1902, 136, 1676; 1903, 137, 60). In this reaction the acid is reduced by heating the methyl or ethyl ester with sodium in ethyl alcohol and reduction takes place according to the following equations:-

$$R.COOEt + 4Na + 3EtOH \longrightarrow R.CH_2OH + 4EtONa.$$

One gram molecule of the ester is dissolved in three or four times its weight of ethyl alcohol, and slowly dropped on to six atomic proportions of sodium in a reflux apparatus. The rate of flow is maintained so that the mixture keeps boiling vigorously during the addition. After cooling, sufficient water is added to liquify the whole, and the greater part of the ethyl alcohol is distilled off; the newly-formed alcohol is extracted from the residue with ether.

The isolation of the more complex alcohol is only accomplished with difficulty. After the removal of the ethyl alcohol, a hard mass remains which consists of the new alcohol and the sodium residues. This can only be separated by treatment with super-heated steam or by extraction with ether in a

Apart from the reduction of the ester to alcohol, nuclear reduction may also take place. This fact has been established by de Pommereau (Centralblatt, 1922, I. 1105) who found that the reduction of benzoic ester gives hexahydrobenzoic ester as well as small amounts of tetrahydrobenzyl alcohol.

The/

The yield of alcohol obtained from the reduction of the corresponding ester appears to be improved by an increase in the molecular weight of the acid or by unsaturation in the nucleus attached to the acid group (Rupe and Lauger, Helv. Chim. Acta., 1920, 3, 272).

The application of this method to the present synthesis, consists in the attempted reduction of the ethyl ester of diphenylmethane p. carboxylic acid by sodium in alcohol:-

$$C_6H_5CH_2C_6H_4COOEt \longrightarrow C_6H_5CH_2C_6H_4CH_2OH + EtOH.$$

The ethyl ester of this acid was prepared as previously described (see page 97 ) and on fractional distillation it boiled at 180° under 5 mm. pressure.

The reduction of this ester was attempted in ethyl alcohol following the method described by Bouveault and Blanc. The alcoholic solution of the ester was dropped slowly on to sodium, but when the reaction mixture was examined, the residue which was obtained was found on distillation under reduced pressure to consist of unchanged ester. Several reductions were carried through, in which the amount of sodium and ethyl alcohol were increased to give a longer time of reduction, but in each case the ester of diphenylmethane carboxylic acid was recovered over the range 175-183 under 5 mm. pressure.

The difficulty experienced in bring about reduction in this case would appear to be in contradiction of the observation of Rupe and Lauger who stated that the reduction proceeded more readily with increase in the molecular weight of the acid portion of the nucleus. At this stage of the work, however, more hopeful results were being obtained by the reduction of the keto-alcohol, benzoylbenzyl alcohol, with sodium in amyl alcohol, and the investigation of the diphenylmethane p. carboxylic acid was therefore discontinued.

## EXPERIMENTAL.

The ethyl ester of diphenylmethane p. carboxylic acid was prepared from the acid by heating it with ethyl alcohol containing 3% hydrochloric acid (see page 97) and was purified by distillation until a fraction boiling at 180° under 5 mm. was obtained.

The first reduction was carried out with quantities equivalent to those used by Bouveault and Blanc.

10 gms. Ethyl ester of diphenylmethane p. carboxylic acid.
40 gms. ethyl alcohol.
6.5 gms. sodium.

The ester was dissolved in the ethyl alcohol and the solution was dropped slowly from a funnel on to the sodium which was contained in a 250 c.c. flask fitted with a reflux condenser, and protected from the atmospheric moisture by a calcium chloride tube. The rate of flow of the ester solution was contolled so that the mixture was kept boiling vigorously during the addition. After the ester had all been added, the solution was heated externally until all the sodium had dissolved.

On cooling, sufficient water was added to liquefy the whole mass, and the greater part of the ethyl alcohol was removed by distillation. The remaining residues were extracted with ether three times and the excess ether distilled off. On fractionally distilling the ether residues, the ethyl ester was recovered unchanged in a fraction boiling between 175° and 185° under 5 mm. pressure. The fact that the distillate consisted of unchanged ester was established by hydrolysing a small portion with alcoholic caustic potash, and on pouring the alcoholic mixture into dilute/

dilute acid, crystals were obtained which proved to be diphenylmethane p. carboxylic acid. M.P. 156-157°.

Further experiments were conducted in which the proportion of ester to sodium was increased to one molecule of ester to 12 atoms of sodium with corresponding increases in the quantity of ethyl alcohol. These, however, did not prove to be successful since the ester was always recovered unchanged, and as previously explained this method was abandoned in favour of that through the ketonic alcohol p.benzoylbenzyl alcohol.

## III. REDUCTION OF p. BENZOYLBENZYL ALCOHOL.

(1) Preparation of Benzoylbenzyl Alcohol.

(2) Clemmensen Reduction.

(3) Wolff's Reaction.

(d) Reduction by means of sodium in Alcohol.

## PREPARATION OF p.BENZOYLBENZYL ALCOHOL. $C_6H_5CO.C_6H_4CH_2OH$.

The third method of synthesis of p.benzylbenzyl alcohol has for a starting material, the corresponding keto-alcohol, p.benzoylbenzyl alcohol, from which the desired alcohol could conceivably be prepared by reduction of the ketonic grouping. This alcohol may conveniently be prepared from phenyl p. tolyl ketone by side-chain bromination of the methyl group and hydrolysis of the bromide to give the keto-alcohol, p. benzoylbenzyl alcohol. Phenyl p tolyl ketone is best prepared from toluene and benzoyl chloride by the Friedel and Crafts reaction.

(a) $C_6H_5CH_3 + C_6H_5COCl \longrightarrow C_6H_5CO.C_6H_4CH_3$

(b) $C_6H_5CO.C_6H_4CH_3 + Br_2 \longrightarrow C_6H_5CO.C_6H_4CH_2Br + HBr$.

(c) $C_6H_5CO.C_6H_4CH_2Br \longrightarrow C_6H_5CO.C_6H_4CH_2OH$.

The method which follows, is based on the synthesis of this alcohol by Bourcet (Bull. Soc. Chim. (3) 15 947) with several modifications which were made as the result of practical experience.

(a) Phenyl p. tolyl ketone.

This compound was prepared by the Friedel and Crafts reaction between toluene and benzoyl chloride in the presence of aluminium chloride. No carbon disulphide was added as this caused the reaction to become too vigorous and made it difficult to control. A large excess of toluene was used, and this helps to prevent the formation of viscous products.

The reaction was carried out in a 2 litre flask, fitted with reflux condenser, and a dropping funnel through which/

which the benzoyl chloride was added. As sometrouble was experienced due to the use of impure benzoyl chloride, it is best that this material be distilled before use, collecting the fraction boiling between 192 and 197. The toluene, also was dried over sodium and redistilled. B.P. 110°.

1 litre dry toluene
100 gms. Benzoyl chloride.
50 gms. Aluminium chloride.

The dry toluene was poured on to the powdered aluminium chloride and the benzoyl chloride added from a dropping funnel to the flask with repeated shaking. This addition took about an hour, as the reaction soon became vigorous and large volumes of hydrochloric acid gas were evolved. The temperature was not allowed to exceed 25° by cooling the flask in a water-bath, since too high a temperature at this stage of the action causes formation of viscous products. When the reaction was finished, the mixture was boiled for several minutes and more hydrochloric acid gas was evolved. After cooling, the reaction mixture was washed with a large excess of water containing a little hydrochloric acid to destroy the aluminium chloride, and the solution dried over anhydrous sodium sulphate. The large amount of unchanged toluene was distilled off, and the ketone distilled, the range between 320 and 330° being collected. On cooling, the distillate solidified and was recrystallised from alcohol. M.P. 56°. Yield = 80 gms.

(b) Bromide of phenyl p. tolyl ketone. $C_6H_5CO.C_6H_4CH_2Br$.

Bromination of this ketone was carried out in a retort heated in an oil bath to 150°, and as side-chain bromination was required, no catalyst was necessary. Equimolecular quantities of ketone and bromine were taken.

20 gms. Phenyl p. tolyl ketone.
16 gms. Bromine.

It is preferable that the reaction be carried out in successive small amounts as above, than in one large experiment, as this helps to minimise the formation of the dibromO derivative.

The bromine was added drop by drop to the heated ketone and the large volumes of hydrobromic acid, formed during the bromination were led into the exhaust vent of the fume-chamber. On cooling a viscous mass was obtained, which on freeing from hydrobromic acid by washing with water, was crystallised from alcohol or ether in white needles.
M.P. 96 Yield = 22 gms.

(c) p.Benzoylbenzyl Alcohol.

The hydrolysis of the bromide of phenyl p. tolyl ketone to benzoylbenzyl alcohol can be effected in two ways.

(1) By boiling with dilute potassium carbonate under reflux, the bromide is hydrolysed with formation of potassium bromide. 25 gms. of bromide were boiled with 2 litres 2% potassium carbonate. After 10 hours the larger portion of the bromide had been dissolved and the solution reduced to half its volume, when the benzoylbenzyl alcohol crystallised out on cooling. M.P. 48°.

The/

The drawback to this method is the long time required for hydrolysis and the inconvenience of working with large volumes of liquid which require to be concentrated before satisfactory yields are obtained.

(2) A more convenient method of hydrolysis is through the acetate and subsequent hydrolysis of this derivative with potassium hydroxide. 25 gms. bromide dissolved in the minimum amount of hot alcohol were boiled for 2 hours with 50 ml. of saturated potassium acetate solution, when the bromine separated out as potassium bromide. This was filtered off, leaving the alcoholic solution of the acetate of the required alcohol. This acetate was hydrolysed by heating for 5 minutes with 100 ml. of 30% caustic potash, and the alcohol obtained by pouring the mixture on to crushed ice. At first the alcohol was usually obtained as an oil, owing to its low melting point, but it was readily crystallised by boiling an ethereal solution with Norite, and allowing to cool. Yield = 19 gms. recrystallised alcohol.

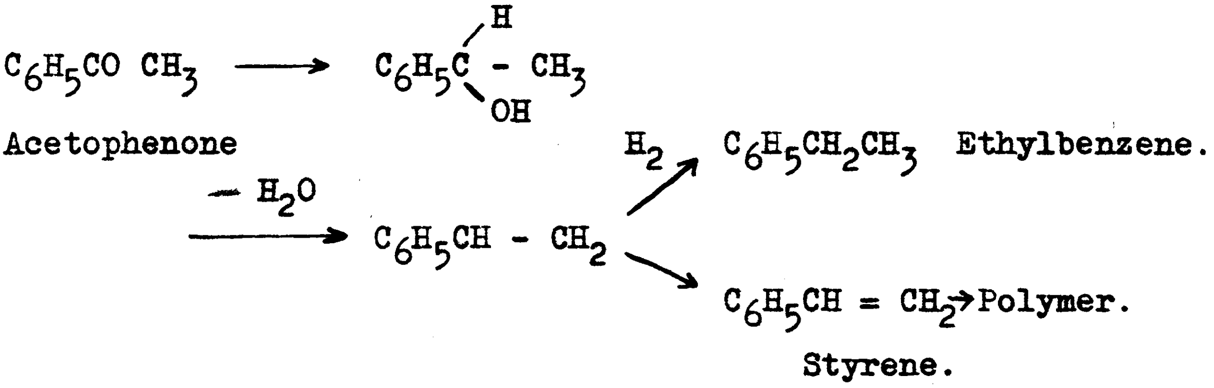
## CLEMMENSEN REDUCTION.

The Clemmensen method of reduction is commonly used for the conversion of a ketonic to a methylene group, but the literature contains no references to its use in the reduction of keto-alcohols. In its application to the reduction of benzoylbenzyl alcohol, the reaction was carried out in the usual way by boiling the alcohol with hydrochloric acid and amalgamated zinc under reflux on a water-bath until all the zinc was dissolved. This alcohol dissolves readily in hot water, but the addition of hydrochloric acid to give a 1:1 mixture of acid and water caused its immediate precipitation.

Because of its low melting-point, p.benzoylbenzyl alcohol readily became liquid, and floated on top of the acid, thus preventing intimate contact of the alcohol with the nascent hydrogen liberated by the zinc. In order to prevent this, the reaction mixture was agitated with a mechanical stirrer, fitted with a mercury seal, and after 12 hours reduction under these conditions, a solid product of low melting point was isolated from the acid mixture on cooling. This product, unlike the original benzoylbenzyl alcohol was insoluble in ethyl alcohol, but dissolved readily in chloroform and dioxan. This substance could not be distilled, and when purification from these solvents was tried, an oily product was always formed.

Considerable light on the probable course of this reaction is obtained from the work of Steinkoff and Wolfram (Annalen, 1922, 430, 124) on the reduction of acetophenone to ethylbenzene by the Clemmensen reaction. These authors found that the best method for carrying out this reduction was to add/

add the amalgamated zinc to a mixture of hydrochloric acid and water (1:1), which was heating under reflux with constant agitation. When the strength of the acid was reduced to one part of acid to two parts of water, the yield of ethyl benzene was lowered by over 50%. In addition, Steinkoff and Wolfram isolated from the residues of the reaction, the pinacol of acetophenone and also a dehydrated polymerisation product to which they assigned the formula $(C_8H_8)_x$. They suggest the following mechanism for these reactions:-



$$C_6H_5CO\ CH_3 \longrightarrow C_6H_5C(H)(OH) - CH_3$$

$$\xrightarrow{-H_2O} C_6H_5CH - CH_2 \begin{cases} \xrightarrow{H_2} C_6H_5CH_2CH_3 \\ \longrightarrow C_6H_5CH = CH_2 \rightarrow \text{Polymer.} \end{cases}$$

No Styrene was isolated from the reaction mixture but only the polymerisation product $(C_8H_8)_x$, which they assumed to have been formed from the styrene.

On the analogy of the scheme devised by these authors, the reduction of benzoylbenzyl alcohol, besides giving the desired "methylene" in place of the ketonic group, would also result in the formation of a polymerisation product.

In later experiments in which the reduction of acetophenone was carried out in absolute alcohol (Annalen, 1922, 430, 157). Steinkopf and Wolfram report that they obtained no ethylbenzene but that the product consisted of a mixture of acetophenone pinacol and the polymerisation product $(C_8H_8)_x$.

This/

This modification was tried with benzoylbenzyl alcohol since it overcame the problem of the insolubility of the alcohol in aqueous hydrochloric acid, and the product was the same as that obtained previously (page 110). Owing to the difficulty of purification, this substance was not analysed, and could not be identified, but from a physical examination it appeared to be resinous in character.

From these results it would appear that polymerisation had taken place by both methods of reduction of benzoylbenzyl alcohol. According to the scheme of Steinkopf and Wolfram, the first stage in this polymerisation is the removal of the elements of water which could take place, not only within the molecule as was the case with acetophenone, but also by inter-molecular condensation through the alcoholic group. By such a mechanism a product of a complex nature would be formed.

EXPERIMENTAL.

200 gms. Granulated Zinc.
400 mls. 5% Mercuric chloride solution.
15 gms. p: Benzoylbenzyl alcohol.
200 mls. Hydrochloric acid.

To the amalgamated zinc, prepared by allowing the granulated zinc to stand for one hour in a 5% solution of mercuric chloride, 200 mls. of a mixture of equal quantities of concentrated hydrochloric acid and water were added, the solution stirred mechanically and heated on a water-bath, it became liquid and floated on the surface, but with rapid agitation it formed an emulsion with the acid.

The action was continued for 12 hours, and after 2 hours heating 200 mls. acid (1:1) were added to maintain the acid strength. On cooling it was found that the product had separated as a solid cake which floated on the surface of the acid layer. This was separated by filtration, crushed under water to free it from acid, and dried.

When purification was attempted by solution in dioxan and treatment with Norite, the precipitate came down as an oil, and was only obtained in the solid state after exhaustive drying under vacuum. After similar treatment in chlor form and precipitation with petroleum ether, an oil was again formed which only solidified after prolonged drying. The melting-point of the solid was indefinite being over the range 40-45°, and when further purification was tried by distillation, the substance was completely charred before any distillate could be collected.

The other method of carrying out this Clemmensen reduction makes use of absolute alcohol as a solvent.

400 gms. Absolute Alcohol.
80 gms. Amalgamated Zinc.
30 gms. Benzoylbenzyl Alcohol.

The alcohol was saturated with dry hydrochloric acid gas, and as the temperature of the mixture was kept down to 15-20°, over this range there was no reaction, and the benzoylbenzyl alcohol was recovered unchanged.

When the reaction temperature was raised to 30°, there was rapid evolution of hydrogen from the zinc, and in a short time an insoluble substance separated out. As there had been considerable loss of hydrochloric acid, in the course of the heating, the absolute alcohol was again saturated with gas, and the process repeated until the zinc was all dissolved.

The acid mixture was poured into water and the insoluble oil, which was precipitated was dissolved in chloroform, and after evaporation of the solvent, was dried under vacuum. The solid which was obtained, melted over the range 41-47°, and was similar to that formed by reduction in aqueous acid, Like that substance it could not be purified for analysis, and as has been previously explained, it was thought to be a polymerisation product formed according to the scheme of reaction suggested by Steinkopf and Wolfram.

## (3) WOLFF'S REACTION.

One of the standard methods for the reduction of a ketonic group to the methylene group is Wolff's reaction, in which the reduction is carried out by means of the hydrazone or semicarbazone of the ketonic compound. Decomposition of these derivatives takes place on boiling with sodium ethylate, e.g.,

$$>C_6H_5CH = N.NH_2 \longrightarrow >C_6H_5CH_3 + N_2$$

$$>C = N.NH.CONH_2 \longrightarrow >C = N.NH_2$$

$$\longrightarrow >CH_2 + N_2$$

The usual treatment consists in boiling the derivative of the ketonic compound with absolute alcoholic sodium ethylate for 6-8 hours at 160-180°. The method has been used for the reduction of aliphatic, aromatic and alicyclic ketones, and even in the case of diketones, but the literature contains no references to its use with keto-alcohols.

The application of this reaction to the present synthesis depends on the reduction of the hydrazone or semicarbazone of benzoylbenzyl alcohol but as neither of these derivatives have been reported in the literature their preparation had first of all to be tried.

The preparation of the hydrazone of benzoylbenzyl alcohol was attempted by the standard method using hydrazine sulphate. The hydrazine sulphate was dissolved in hot water and neutralised with the equivalent amount of anhydrous sodium carbonate, the alcohol added and the mixture shaken up. After allowing the solution to cool, only the unchanged alcohol/

alcohol separated out. Similar experiments were carried out using hydrazine hydrate but the hydrazone could not be prepared, the alcohol being recovered unchanged.

The preparation of the semicarbazone was then tried using semi-carbazide hydrochloride. The first experiments were carried out by dissolving the semi-carbazide hydrochloride in the minimum amount of water, and the free base was liberated by the addition of potassium acetate. The benzoyl-benzyl alcohol was dissolved in ethyl alcohol, and the two solutions mixed together and shaken. However it was found that the water which was used to dissolve the semi-carbazide precipitated the keto alcohol from the ethyl alcohol, and cuased it to float on the top of the reaction solution as an oil.

To avoid this, semi-carbazide hydrochloride was dissolved in alcohol, and alcoholic solution of potassium acetate added, and the potassium chloride filtered off. The alcoholic solution of the keto-alcohol was then added, and the mixture allowed to stand for some time, but even after several days no crystallisation took place. This solution contained a large amount of excess alcohol due to the low solubility of semi-carbazide hydrochloride, and was concentrated by heating gently under reduced pressure. On further evaporation only crystals of the unchanged keto-alcohol could be obtained.

The volume of alcohol required was reduced by using semi-carbazide free base, obtained by evaporating a solution of semi-carbazide hydrochloride to dryness after neutralisation with anhydrous sodium carbonate. Another method which was used was to boil the solution containing the semi-carbazide/

semicarbazide and the keto-alcohol, and then add to the hot solution a drop of dilute hydrochloric acid as catalyst. In none of these reactions was any product other than the unchanged alcohol recovered from the solution.

As a result of the failure to prepare either of the required derivatives of the benzoylbenzyl alcohol, it was not possible to attempt reduction by means of Wolff's reaction.

### (4) REDUCTION OF p. BENZOYLBENZYL ALCOHOL WITH SODIUM IN ALCOHOL.

The reduction of the ketonic group of benzoylbenzyl alcohol can be attempted in various ways, and since the standard Clemmensen reduction did not prove successful, the displacement of the oxygen atom by hydrogen was tried by reduction with sodium in absolute alcohol, according to the method as employed by Kermack, Perkin and Robinson (J.C.S. 1924, 121, 1872). A similar method was used by Klages and Allendorf (Ber., 1898, 31, 999) for the reduction of phenyl p. tolyl ketone to benzyltoluene. It consists in boiling a solution of one part of ketone in ten parts of absolute alcohol with one part of sodium until all the sodium has dissolved. In the case of benzoylbenzyl alcohol, allowance would require to be made for the formation of the sodium salt of the alcohol.

When reduction was carried out by this method, and the reaction mixture examined, it was found that, in addition to a large amount of unchanged alcohol, a pale yellow oil was formed which did not crystallise even on cooling in ice. This oil, on fractional distillation under reduced pressure, yielded in addition to a further quantity of the original alcohol, a liquid boiling between 140° and 145° under 3 mms.

Further reductions in absolute alcohol continued to give large fractions of unchanged benzoylbenzyl alcohol, in spite of the use of atomised sodium and the prolongation of the time of reaction by the addition of alcohol and sodium to the mixture. Under these circumstances it was thought that the temperature of reduction was not sufficiently high and so ethyl alcohol was replaced by the higher-boiling amyl/

amyl alcohol.

The use of ethyl and amyl alcohol in ketonic reductions has been investigated by Klages and Allendorf, and from their researches these authors concluded that, while the higher temperature of reduction in amyl alcohol was necessary in some cases, the product from a sodium reduction in this alcohol was usually contaminated either with a pinacol or a secondary alcohol, and that in general the use of ethyl alcohol resulted in the formation of a purer product.

The reduction of benzoylbenzyl alcohol by sodium in amyl alcohol, gave an oil similar to that formed in ethyl alcohol, and after repeated fractionation, a colourless liquid, B.P. 143-145 under 4 mms., was obtained which on analysis had the composition, C = 86.3%, H = 9.1% and O = 4.6%. This analysis shows the formation of a product too rich in carbon and hydrogen when compared with the desired compound, benzylbenzyl alcohol, which had a composition of C = 84.85%, H = 7.07%, O = 8.08%. Since the starting material, benzoylbenzyl alcohol has a percentage analysis of C = 79.24, H = 5.66%, O = 15.1%, these figures would seem to show that reduction of the ketonic group had taken place. The boiling-point of benzylbenzyl alcohol, however, as reported by Wertyporoch and Farnik (see page 73) is 155° under 4 mm., and this is ten degrees above that obtained for the reduction product.

From the above facts it would appear that the treatment of benzoylbenzyl alcohol with sodium in alcohol, had caused some reduction to take place, although the analyses still left the identity of the product open to doubt, and as a result, an attempt was made to form the ether/

ether of this reduced product. This was first tried by heating the liquid with anhydrous zinc chloride according to the method of Errera (Gazzetta, 18.24) but this reagent was not powerful enough, and the starting product could be recovered unchanged.

Phosphorus pentoxide was used in place of zinc chloride, but no appreciable action took place until the mixture of the reduction product and the powdered pentoxide had been heated for a short time at 200°. When the mass was freed from dehydrating agent by washing with water, a solid product remained in place of the liquid starting material. None of the original substance was recovered and the solid which remained was very insoluble.

Unlike the substance which was formed by the action of sulphuric acid and dibenzyl ether, this material did not dissolve in dioxan or any of the usual range of organic solvents, nor did it show any signs of softening within the melting range of that product. As it was so insoluble, it could not be purified sufficiently for analysis but a physical examination would seem to indicate that it does not resemble closely the product which it is desired to synthesise. In any case the uncertainty regarding the composition of this reduction product would prevent this result from being taken as conclusive.

Several dehydration experiments were carried out using sulphuric acid in place of phosphorus pentoxide. With dilute acid the reduction product was unaffected, but when 80% sulphuric acid was used, there was a vigorous reaction and a solid product separated when the acid mixture was poured into water. As in the previous case with phosphorus pentoxide, this material showed extreme insolubility/

insolubility, and could not be purified.

These reactions with phosphorus pentoxide and sulphuric acid have shown that in the presence of a strong dehydrating agent, the reduction product of benzoylbenzyl alcohol with sodium in amyl alcohol could react in a similar manner to benzyl alcohol; however, as the exact nature of the reduction product was not known, the reduction of this ketonic alcohol was discontinued, and another method of synthesis was adopted.

## EXPERIMENTAL.

The reduction of p. Benzoylbenzyl alcohol was first attempted with absolute alcohol using the following quantities.

10 gms. p. Benzoylbenzyl alcohol.
12 gms. Sodium.
100 gms. Absolute Alcohol.

The benzoylbenzyl alcohol was dissolved in the absolute alcohol, which was heated in a bolt-head flask on a water-bath. When all the sodium had dissolved the reaction mixture was poured into water to destroy the sodium ethylate, dilute hydrochloric acid added, and the acid liquor extracted with ether.

When the excess ether had been removed, the remaining liquid was redissolved in ethyl alcohol, purified by boiling with Norite and the solution concentrated by distilling off the alcohol. After cooling in a freezing mixture, the alcoholic residues still remained liquid. The last traces of alcohol were removed by allowing the liquid to stand for some time in vacuum over calcium chloride, but even on seeding, no crystals of unchanged alcohol were obtained. Yield of liquid product = 9 gms.

This liquid was then separated into two fractions by distillation.

| | | | |
|---|---|---|---|
| 1st Fraction | 130-135 | under 2 mm. | 3 gms. |
| 2nd Fraction | 140-180 | under 2 mm. | 5 gms. |

Since the boiling point of benzoylbenzyl alcohol is not reported in the literature, a fresh sample of the alcohol was fractionally distilled and gave a steady boiling range of 151-155° under 2 mms.

The/

The second fraction obtained above was redissolved in ethyl alcohol and after being treated several times with Norite, gave a crystalline deposit which was found to be unchanged alcohol. M.P. 47-48. Yield = 4 gms.

The first and lower boiling fraction was treated in a similar manner, but it still remained liquid. This depression of the boiling-point is consistent with the change in the physical constant which usually results from the replacement of oxygen by hydrogen in the molecular structure, and would seem to indicate that reduction had taken place.

Several experiments were carried out in which the time of the reduction was varied, but this did not increase the yield of the reduction product. Atomised sodium, made by shaking molten sodium in a closed tube under boiling xylene was used to increase the vigour of the reduction. In all cases, however, approximately half of the benzoylbenzyl alcohol was recovered unchanged.

Since it was impossible to increase the temperature of the reduction using ehtyl alcohol, the higher boiler amyl alcohol was substituted in the experiments which follow,

| | |
|---|---|
| 10 gms. | Benzoylbenzyl alcohol. |
| 100 gms. | Amyl alcohol. |
| 8 gms. | Sodium. |

The reduction was carried out in a similar manner to that with ethyl alcohol, and in this case atomised sodium was not necessary since the sodium became molten at the temperature of boiling amyl alcohol. After all the sodium had dissolved, the reaction mixture was shaken with water and dilute hydrochloric acid added until an acid reaction to Congo Red was obtained, and the aqueous liquer extracted with ether.

It was found that this procedure was preferable to that of Klages and Allendorf, which consisted in destroying the sodium amylate by passing carbon dioxide through the alcoholic solution and filtering off the precipitated sodium carbonate. This process was slow and laborious because of the viscous nature of the amyl alcohol solution.

The amyl alcohol, which boiled at 42° under 4 mms. pressure, was removed by distillation, and the remainder of the distillate was collected between 140° and 160° under 4 mms. Fractionation of this liquid resulted in the recovery of 3.5 gms. of benzoylbenzyl alcohol, and a constant boiling distillate was collected at 143-145° under 4 mms. This distillate gave the following analysis as compared with the percentage composition for the possible products.

| | | C. | H. | O. |
|---|---|---|---|---|
| Reduction Product | | 86.3 | 9.1 | 4.6 |
| Benzoylbenzyl Alcohol | $C_6H_5CO.C_6H_4CH_2OH$ | 79.24 | 5.66 | 15.10 |
| Benzylbenzyl Alcohol | $C_6H_5CH_2C_6H_4CH_2OH$ | 84.85 | 7.07 | 8.08 |
| p.Hydroxy methyl-benzhydrol | $C_6H_5CH(OH)C_6H_4CH_2OH$ | 78.5 | 6.53 | 14.97 |

From these figures, it would appear that reduction of benzoyl-benzyl alcohol had taken place by this method, but no more definite analyses could be obtained after repeated fractionation of the reduction product. The analysis of the distillate shows a percentage of carbon and hydrogen in excess of that required by benzylbenzyl alcohol. This discrepancy, however, may be caused by the presence in the distillate of small amounts of material rich in carbon, produced by the condensation of the alcoholic group in the starting product by loss of water, in the presence of the dehydrating agent, sodium.

Because/

Because of the close approximation of the analysis of this reduction product to that of the desired alcohol, further reductions were carried out by this method, and the etherification of the product attempted by dehydration with various agents.

The first dehydrating agent with which ether formation was tried, was anhydrous zinc chloride, according to the method of Errera (Gazzetta, 18, 24).

5 gms. Reduction Product
5 gms. Powdered zinc chloride.

The reactants were heated together in a small flask for some time at 200°, and above this temperature, decomposition of the liquid took place. There were no visible indications of reaction, and when the mixture was freed from zinc chloride by washing with water, there remained an oily residue which on extraction with ether and fractional distillation, was shown to be unchanged starting material.

Heating of the reaction mixture to temperatures in excess of 200°, with the consequent risk of decomposition, proved to be of no practical value, as no other product could be isolated by fractional distillation under reduced pressure.

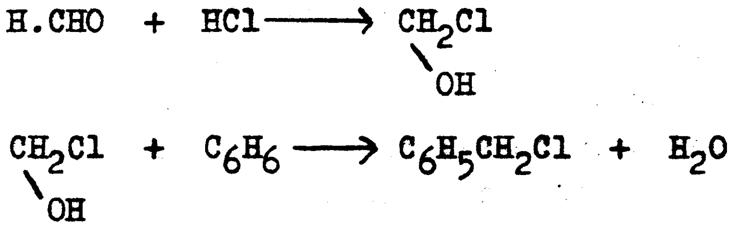
Since the failure to bring about reaction may have been caused by the fact that the dehydrating action of zinc chloride was not sufficiently vigorous, several experiments were carried out using phosphorus pentoxide, with the additional precaution that the reaction flask was closed with a calcium chloride tube to prevent access of atmospheric moisture.

No action took place below 100$^{\circ}$, but when the temperature was maintained at 150$^{\circ}$ for 15 minutes, a solid product remained after the excess phosphorus pentoxide had been removed with water. This dark brown substance was very insoluble, and neither dissolved in the usual range of organic solvents nor showed any of the physical characteristics of the product which it is desired to synthesise. As no solvent was found for this material, it could not be satisfactorily analysed and its exact nature was not determined.

Etherification was also attempted using dilute sulphuric acid, but unlike the actions described by Oddo (Gazzetta, 1901, 241) no catalytic etherification took place. When the reduction product was added slowly to warm 80% sulphuric acid, there was an immediate reaction and a solid material was obtained when the acid was removed by pouring the mixture into water. This solid closely resembled that formed with phosphorus pentoxide, and like that substance could not be purified for analysis because of its extreme insolubility.

## IV. BLANC'S REACTION.

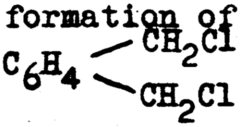
The synthetic preparation of p. benzylbenzyl alcohol was further attempted using a method suggested by Blanc's reaction by which he caused the substitution $CH_2Cl$ groups in an aromatic hydrocarbon nucleus, e.g. he prepared benzyl chloride from benzene in 80% yield (Bull. Soc. Chim. 1923 (4) 33, 313). The chlorination is effected by hydrochloric acid gas and formaldehyde in the presence of zinc chloride.



$$\mathrm{H.CHO} + \mathrm{HCl} \longrightarrow \underset{\diagdown\mathrm{OH}}{\mathrm{CH_2Cl}}$$

$$\underset{\diagdown\mathrm{OH}}{\mathrm{CH_2Cl}} + C_6H_6 \longrightarrow C_6H_5CH_2Cl + H_2O$$

The dry gas was passed into a mixture of benzene, formaldehyde and powdered zinc chloride until the hydrochloric acid was no longer absorbed. On allowing the mixture to settle, two layers separated out, the top layer containing the benzyl chloride which was obtained by washing the fraction by decantation with water, and separated from the unchanged benzene by distillation.

In addition to the formation of benzyl chloride, the para-dichloro derivative  $C_6H_4\begin{matrix}\diagup CH_2Cl\\ \diagdown CH_2Cl\end{matrix}$ was also isolated from the distillate. The percentage of these higher products in the reaction mixture depends on the proportion of zinc chloride used, e.g. in the case of the production of benzyl chloride from benzene, it was found that the best results were obtained when equal quantities of formaldehyde and zinc chloride were taken. The amounts added were/

were equal to 1/10th the weight of the benzene, and with these proportions only small amounts of the higher products could be isolated from the reaction mixture. When, however the quantity of zinc chloride was increased, the proportion of these higher products was also considerably increased.

This reaction may be sucessfully carried out using 40% Formalin and in this case the amounts of the reacting constituents were altered to preserve the ratio of formaldehyde to the zinc chloride; thus instead of equal quantities of these materials, the proportion was altered to 75 gm. 40% Formalin and 100 gm. zinc chloride to 400 gms. of benzene. It was found that the percentage of diphenylmethane in the final product increased with the time of reaction and it is probable that this is due to the fact that the zinc chloride was acting like aluminium chloride in a Friedel and Crafts reaction, i.e.

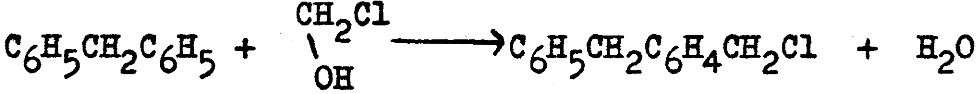
$$C_6H_5CH_2Cl + C_6H_6 \longrightarrow C_6H_5CH_2C_6H_5 + HCl$$

Also it was necessary to make sure that all the zinc chloride was removed by washing with water, as during the final distillation stage traces of this compound gave rise to resins.

With the higher hydrocarbons, toluene and xylene, the substitution by the $CH_2Cl$ group took place readily, with the formation of very few by-products, the chief impurity being the dichloro-derivatives.

By the use of this reaction, it was thought possible that the desired benzylbenzyl alcohol could be prepared by the hydrolysis of the corresponding aryl chloride by means of potassium acetate and caustic potash. For/

For this purpose the starting material was diphenylmethane which could conceivably be converted into benzylbenzyl chloride according to the following equation.



$$C_6H_5CH_2C_6H_5 + \begin{array}{c} CH_2Cl \\ \backslash \\ OH \end{array} \longrightarrow C_6H_5CH_2C_6H_4CH_2Cl + H_2O$$

In the original experiments using benzene, in which the proportion of zinc chloride was increased causing the formation of large amounts of diphenylmethane, Blanc gave no details of the reaction which would serve to indicate that the diphenylmethane in its turn had been chlorinated, showing the greater stability of diphenylmethane as compared with benzene under these conditions. The fact that diphenylmethane did not show the same reactivity towards the chlorinating agent as was shown in the case of toluene and xylene, was confirmed by experiments carried out under the same conditions, i.e. at a temperature of 60° with the passage of hydrochloric acid gas for ½ hour, the diphenylmethane was unaltered and could be recovered completely from the reaction mixture. Formaldehyde was used in its three forms, as 40% formalin, paraformaldehyde and trioxymethylene, but in no case was there any reaction under these conditions.

A series of experiments was conducted in which the temperature of the reaction and the time of passage of the hydrochloric acid was progressively increased by intervals of 10° and 30 minutes until they reached a limit of 150° for 3 hours; when these conditions had been reached, and the unchanged diphenylmethane had been distilled off up to a temperature of 150° under 5 mm., there still remained a residue which could not be distilled without decomposition. Further reactions with more stringent conditions did not give any more satisfactory results. The oil which was left after the/

the removal of the diphenylmethane was soluble in benzene and was purified from this solvent by treatment with Norite. Evaporation of the excess benzene did not cause the liquid to crystallise, and after standing for some time it became resinous in character. On testing in the usual manner by fusing a small bead of the substance with sodium, it was found to contain chlorine, but it was not possible to extract from the resin a fraction of sufficient purity for analysis. The boiling point of the small amount of material, siolated by Wertyporoch and Farnik (Annalen, 1931, 491, 271) from the action of benzyl chloride on aluminium chloride, and thought by these authors to be chlormethyl diphenylmethane, is given as 160° under 2 mm. Under these conditions no distillate could be obtained by prolonged heating of the oily resin, since decomposition set in above 150°.

From the fact that chlorine was detected in the final product it may be concluded that chlorination had taken place to a certain degree. However at the high temperature necessary to bring about chlorination, this product would be free to react with the unchanged diphenylmethane in the presence of anhydrous zinc chloride in the same way as reaction would take place in the presence of aluminium chloride. This side-reaction was noted by Blanc in his original research on the preparation of benzyl chloride from benzene and affords a satisfactory explanation of the resinous nature of the final product.

## EXPERIMENTAL.

The reaction was carried out in a bolt-head flask fitted with a mechanical stirrer closed by a mercury seal and with an inlet-tube for the hydrochloric acid gas which was bubbled through the reaction mixture. The gas escaped through a reflux condenser to which was fitted a calcium chloride tube, and was led into the exhaust vent of a fume chamber. The formaldehyde was first used in the form of 40% formalin, and the diphenylmethane was distilled under reduced pressure before use (B.P. 120° at 5 mm.) In the initial experiments the quantities of the reacting constituents were kept in the same molecular proportions as in the original reactions with benzene.

| | |
|---|---|
| 30 gms. | Diphenylmethane. |
| 8 gms. | 40% Formalin. |
| 12 gms. | Zinc Chloride. |

The zinc chloride in powdered form was added to a mixture of diphenylmethane and formalin heated to 60° on a water-bath and the contents of the flask stirred rapidly as the diphenylmethane and the formalin were not miscible. Hydrochloric acid gas dried by passing through a sulphuric acid bubbler was lead into the agitated mixture for half an hour the temperature being kept at 60°. When the excess zinc chloride had been removed by filtration, and the aqueous fraction separated off, the residue was washed several times with water to remove the last traces of zinc chloride, as this salt may cause resinification during the subsequent distillation. The liquid, now free from zinc chloride, was extracted with a little ether, and dried with anhydrous sodium sulphate. The ether was removed on a water-bath/

water-bath and the residue transferred to a Claisen-flask fitted with a fractionating column on the side-arm. On distillation it was found that the diphenylmethane had been recovered unchanged, leaving only a small residue on the bottom of the flask. Yield of diphenylmethane = 27 gms. collected between 120-130 under 5 mm. pressure.

A series of similar experiments in which modifications in the proportions of the reacting constituents and the conditions of reaction were made, were carried out by the above method. The amounts of zinc chloride and 40% formalin were gradually increased until they were in equi-molecular proportions with the diphenylmethane, but the diphenylmethane was recovered unchanged. Increase of the temperature to 140°, and continued passage of the gas for varying periods of time up to 3 hours produced no reaction, and as a result, the formalin was replaced by paraformaldehyde.

II. 50 gms. Diphenylmethane.
15 gms. paraformaldehyde.
15 gms. zinc chloride.

Since the paraformaldehyde and the zinc chloride were both solids, the diphenylmethane was first melted and the two solids in powder form were added slowly to the liquid which was stirred sufficiently rapidly to maintain the solids in suspension. The temperature was kept steady at 80°, and the hydrochloric acid gas passed for half an hour. On working up the reaction mixture in the usual way and distilling off the unchanged diphenylmethane, a residue boiling above 150° under 5 mm. pressure still remained in the flask. From this liquid a small fraction was obtained between 150° and 170°, but this was found to consist mainly of impure diphenylmethane. The greater portion of this high-boiling/

high-boiling constituent still remained in the flask and did not distil below 200° under 2 mm. pressure. Above this range, decomposition and charring became excessive and recourse had to be made to fractional crystallisation, but with little success. Yield of high-boiling product = 6 gms.

Further experiments using varying proportion of paraformaldehyde and zinc chloride gave a similar high-boiling residue which could not be distilled. In these reactions distillation was stopped at 200°, as at that temperature the last trace of diphenylmethane had been removed. Special care was taken to make sure that the distillate was washed free from zinc chloride and hydrochloric acid, as this was thought to be a likely cause of the charring at the higher temperatures of distillation, but even with this precaution no distillate could be obtained. The residues in the flask were taken up in benzene, and purification attempted by repeated treatment of the solution with Norite under reflux. When the benzene solution was concentrated, no crystals separated out but after a time an oily deposit settled on the bottom of the flask. When this oil was kept under vacuum for a few days to remove the last traces of benzene it became resinous in character and showed no tendency to crystallise.

Repeated purification with Norite in a variety of solvents did not effect any improvement and the product could not be purified sufficiently for analysis. The presence of chlorine in this compound was shown by a positive test which was obtained when a small bead of the material was heated with sodium, and the aqueous extract treated with silver nitrate and nitric acid.

Despite/

Despite the impure state of the product, an attempt was made to replace the chlorine which had been shown to be present, with hydroxyl groups by hydrolysis with a saturated alcoholic solution of potassium acetate, i.e. $R.CH_2Cl \rightarrow R.CH_2OH$. This did not prove effective as the resinous product was only slightly soluble in absolute alcohol. A more suitable solvent was sodium-dried dioxan which dissolved both the chlorinated product and the potassium acetate. After boiling the mixture under reflux for several hours, only a few crystals of potassium chloride separated, showing that the amount of p-benzylbenzyl bromide present had been small. In these circumstances further hydrolysis with caustic potash was not attempted.

III.

A third form of formaldehyde, trioxymethylene was then used in the reaction. This was prepared by the method of Auerbach and Barschall from 40% Formalin (Chem. Zentr., 1907 (2), 1734).

By shaking formalin and concentrated sulphuric acid together in the proportion of four volumes of acid to ten volumes of formalin, a white solid, β. polyoxymethylene at once separated. This was filtered off, washed free from sulphuric acid with water and dried. 100 c.c. of formalin yielded 21 gms. polyoxymethylene by this treatment.

This dried material was then sublimed from a glass-retort, heated in a solder-bath, and was collected in a receiver containing a little water and evolved in ice. The liquid product was distilled under reduced pressure and the crystals which separated were recrystallised from ether. Colourless needles. M.P. 63-64°. Yield 15 gms.

Chlorination of diphenylmethane was attempted with the product, using quantities of the reactant materials similar/

similar to those employed in the reaction with paraformaldehyde.

50 gms. Diphenylmethane.
15 gms. Trioxymethylene.
15 gms. Zinc Chloride.

The reaction was carried through as previously described, the temperature being varied between 80° and 160° in successive experiments, above which loss of trioxymethylene occurred due to sublimation. Under these conditions no chlorination took place, and the diphenylmethane was completely recovered by distillation as was the case with the reactions in which 40% formalin was used.

## V. STEPHEN REACTION.

An alternative synthesis which was used in an attempt to prepare p-benzylbenzyl alcohol was through the corresponding aldehyde by means of the Stephen reaction. The basis of this method is the conversion of the nitrile through the imino chloride into an aldehyde with the same number of carbon atoms. The most suitable reducing agent is anhydrous stannous chloride dissolved in ether saturated with hydrogen chloride. The method as described by Stephen (J.C.S. 1925, 127, 1874) consists in suspending finely powdered anhydrous stannous chloride in dry ether which is then saturated with dry hydrochloric acid gas. The nitrile is added to this solution with vigorous shaking and after a few minutes separation begins of the aldimine stannichloride to which Stephen assigns the formula, $(R.CH{:}NH,HCl)_2\ SnCl_4$

After separation of this salt by filtration, it is hydrolysed in warm water and the aldehyde may be removed by distillation in steam or by extraction with a solvent.

In this synthesis, the starting material was phenyl p-tolyl nitrile and the subsequent scheme of reactions would then be as follows:-

$$C_6H_5CH_2C_6H_4CN + HCl \longrightarrow C_6H_5CH_2C_6H_4CCl\ NH$$

$$2.\ C_6H_5CH_2C_6H_4CCl\ NH + SnCl_2 + 4HCl \rightarrow (C_6H_5CH_2C_6H_4CH{:}NH,HCl)_2SnCl_4$$

$$\xrightarrow[\text{with warm water}]{\text{Hydrolysis}} 2\ C_6H_5CH_2C_6H_4CHO.$$

From this aldehyde, the desired alcohol might readily be obtained by the Cannizzaro Reaction, along with an equal quantity of diphenylmethane p. carboxylic acid, whose properties are known and which could be separated from the mixture.

Before/

Before attempting reactions involving phenyl p. tolyl nitrile, a series of preparations were carried through using benzonitrile. From these it was learned that the yield of aldimine stannichloride depended chiefly on the purity of the stannous chloride and the use of sodium dried ether, as the complex salt was easily soluble in water.

Stephen in his earlier work used anhydrous stannous chloride made by fusing the crystalline variety until the temperature reached 180°. This product contained some stannous oxide which was removed by dissolving the fused mass in pyridine. Solution took place with evolution of heat, and the insoluble stannous oxide was filtered off. The filtrate deposited the double complex $SnCl_2\ 2C_6H_5N_1$ and when this compound was heated under reduced pressure, the pyridine was removed and the anhydrous stannous chloride remained.

The best method for the preparation of anhydrous stannous chloride for this reaction is by shaking the crystalline form with two molecules of acetic anhydride (Stephen, J.C.S., 1930, 132, 2786) Dehydration is almost complete, and the anhydrous salt separates on cooling. This method is preferable to the fusion method and the product obtained is much purer. Using this purification of stannous chloride, the aldimine stannichloride was obtained from benzonitrile in theoretical yield, and the yield of aldehyde in the hydrolysis of this salt with warm water, was over 90%.

When this reaction was applied to the case of phenyl p. tolyl nitrile, it was found that the yield of the stannichloride complex was very small, and that on hydrolysing this salt with warm water, and extracting the aqueous liquor with ether, no aldehyde could be detected by means of saturated/

saturated sodium bisulphite.

In order to improve the yield of tin salt, the ether was first purified by shaking with dilute potassium permanganate solution and then drying with soidum. By this means the yield of aldimine stannichloride was increased to 40%, but even when working with these larger quantities no aldehyde was obtained.

The loss of aldehyde in the latter stage of the action was thought to be due to its ease of oxidation, and so the ether used in these experiments was further purified by treatment with aqueous silver nitrate and caustic potash solutions. This procedure (see page 140) completely destroys compounds of the peroxide class while oxidising any aldehydes to acid, which together with any free acid was removed by the excess potash present.

In spite of these precautions, however, no p-benzyl benzaldehyde could be detected in the ether extract after hydrolysis of the tin complex with warm water. The main difficulty arose as a result of the relatively high temperature required for the hydrolysis of the aldimine stannichloride which was unaffected by cold water. The only proof of reaction which could be obtained was the isolation of diphenylmethane p-carboxylic acid from the ether extract.

Various methods were adopted in order to prevent this oxidation of the aldehyde which had been formed, but in no case was it possible to isolate any compound which gave the reactions of an aldehyde. In these circumstances attempts at preparing benzyl benzyl alcohol through the corresponding aldehyde by means of the Stephen reaction were discontinued.

## EXPERIMENTAL.

During the preliminary experiments which were carried out using benzonitrile, it was found that the yield of aldimine stannichloride could be improved on that obtained by Stephen by the use of pure anhydrous stannous chloride. In his original work, Stephen used stannous chloride which had been prepared by fusing the crystalline hydrated salt, and removing the stannous oxide which was formed by extracting the fused mass in pyridine, from which the stannous chloride separates as a double compound, $SnCl_2$, $2C_6H_5N$. When this salt is heated under reduced pressure, the pyridine is removed, and the residue is anhydrous stannous chloride. The following method, however, is preferable as it gives a much purer product (Stephen, J.C.S., 1930, 132, 2786).

Powdered crystalline stannous chloride (1 mol.) was shaken with acetic anhydride (2 mols.) for a few minutes. Dehydration takes place immediately with the evolution of heat and the anhydrous salt separated out and was washed free from acetic acid and anhydride with dry ether. It was recrystallised from alcohol, containing a little acetic anhydride, and was preserved for use as required in a vacuum desiccator.

In the experiments with phenyl p. tolyl nitrile, difficulties were encountered which were thought to be due to the impurities present in the ether used as solvent. These impurities can be partially removed by shaking the ether with a dilute solution of potassium permanganate, but a much more efficient method is that described by Werner (Journal and Proceedings of the Institute of Chemistry, 1935, 113).

The ether is shaken with a solution of aqueous

silver/

silver nitrate and caustic potash. The grey silver oxide which is first formed, quickly becomes dark, giving metallic silver, and by this oxidation destroys hydrogen peroxide and compounds of the peroxide class. Any aldehyde present is oxidised to acetic acid and this together with any free acid, is neutralised by the excess of caustic potash present. One part of hydrogen peroxide in 400,000 parts of ether can be detected by vanadic acid solution, a red colour developing, and aldehyde can be detected by Schiff's reagent. After purification by this method, no reaction was given with either reagent.

The stock solution of anhydrous stannous chloride was prepared by passing the dry hydrochloric acid gas into a mixture of 200 ml. specially purified ether and 50 gms. stannous chloride in a bolt-head flask closed with a rubber stopper and protected at the outlet end with a calcium chloride tube to prevent contamination by atmospheric moisture.

Phenyl p-tolyl nitrile was prepared as previously from p-tolunitrile, and before use it was recrystallised from alcohol and dried in a vacuum desiccator. M.P. 51$^{o}$.

10 gms. Phenyl p-tolyl nitrile.
20 gms. Stannous chloride.
80 ml. dry ethereal hydrochloric acid.

This mixture was thoroughly shaken in a flask protected from the atmosphere by a calcium chloride tube. After a few minutes shaking the nitrile dissolved in the ether, and the solution was allowed to stand. Unlike the reactions with benzonitrile, there was no separation of the aldimine stannichloride until the following day, and even then the yield was very small. After standing for several days 3 gms. of product had separated from the mixture. This experiment was/

was repeated several times, varying the proportion of nitrile to stannous chloride, but in no case was the yield more than 3 gms. of tin salt.

As these yields were too small to permit of a satisfactory examination of the stannichloride complex, a fresh supply of phenyl p-tolyl nitrile was prepared, and another experiment, using the following quantities, was carried out, special care being taken that all the reactants were thoroughly dry.

| | |
|---|---|
| 30 gms. | Phenyl p-tolyl nitrile. |
| 60 gms. | stannous chloride. |
| 150 ml. | dry ether saturated with hydrochloric acid. |

This reaction mixture was shaken vigorously until all the phenyl p-tolyl nitrile was dissolved, and then allowed to stand in a sealed flask for a week. Yield of Tin Complex 15 gms.

This tin complex was decomposed with hot water using the minimum conditions which had been found from a series of small scale experiments which had been carried out using the yields obtained in the previous experiment. The aldimine stannichloride, which had been freed from hydrochloric acid by washing with cold water, was shaken with warm water heated to 60° for 5 minutes, the aqueous mixture cooled in ice, and extracted with ether from which peroxides had been removed. The ethereal extract was dried over anhydrous sodium sulphate, and the ether distilled off until a temperature of 50° had been reached. On allowing the solution to cool crystals separated out, which proved to be diphenylmethane p-carboxylic acid M.P. 150-157°. Yield = 4 gms. Theoretical yield of acid = 6.5 gms.

The/

The ethereal fraction which remained was shaken with freshly prepared saturated sodium bisulphite solution, a small precipitate was obtained, which on treatment with dilute sulphuric acid and extraction of the aqueous liquor with ether, yielded more crystals of diphenylmethane p-carboxylic acid. This showed that the desired p-benzylbenzaldehyde had been formed by the Stephen reaction, but owing to the extreme ease of its oxidation, it was not possible to isolate it in the free state.

Further attempts to prevent this oxidation were made by carrying out the hydrolysis of the stannichloride complex in an inert atmosphere such as nitrogen, and by lowering the temperature at which this hydrolysis was carried out. In the later case it was necessary to prolong the time of contact of tin complex with the warm water, but by neither method was it possible to isolate any constituent other than diphenylmethane p-carboxylic acid. Finally, a Cannizzaro reaction was attempted using the ethereal solution obtained after the hydrolysis of the aldimine stannichloride, but as in the other reactions, no product other than the free acid, could be separated from the reaction mixture. Under these circumstances, the attempt to prepare benzyl-benzyl alcohol by this method was discontinued.

# Treatment of Reaction Product from Dibenzyl Ether with Hydrogen under Pressure.

## TREATMENT OF THE REACTION PRODUCT FROM DIBENZYL ETHER WITH HYDROGEN UNDER PRESSURE.

During recent years, a new technique has been developed for the cleavage of ethers with hydrogen under pressure, and if an ethereal structure for the compound from dibenzyl ether is correct, degradation by this method should be possible.

Ethers react with hydrogen under suitable conditions of temperature, pressure and catalyst in the following manner:-

$$ROR' + H_2 \begin{array}{l} \nearrow \ RH + R'.OH \\ \searrow \ R'H + R.OH \end{array}$$

Such a decomposition has been called hydrogenolysis as distinct from nuclear hydrogenation, which may precede or follow this reaction, if R or R is unsaturated. These reactions have been observed by various authors to occur over nickel, palladium or platinum (Sabatier and Senderens, Bull. Soc. Chim., (3) 33, 616; etc.) but the rapidly increasing importance of Raney nickel made it desirable to survey the behaviour of typical ethers over this catalyst (Chem. Soc., Annual Reports, 1937, 222).

The temperature range over which cleavage of ethers by hydrogenolysis over Raney nickel became reasonably rapid was examined by Duzee and Adkins, (J. Amer. Chem. Soc., 1937, <u>57</u>, 147) and they concluded that this cleavage involved hydrogenolysis and not simply pyrolysis (A) followed by hydrogenation (B), <u>i.e</u>. the cleavage did not take place in the following two stages:-

$$\text{(A)} \quad R.CH_2OR' \rightarrow R.CHO + R'H$$

$$\text{(B)} \quad R.CHO + H_2 \rightarrow R.CH_2OH$$

The benzyl ethers undergo hydrogenolysis at a lower temperature than do other ethers and the cleavage takes place exclusively between the benzyl group and the oxygen at temperatures of 100° to 150°. Within this range a definite conclusion could not be drawn as to the effect of variation in the other constituent upon the temperature of cleavage of benzyl ethers, since traces of impurity in various ethers may account for apparent differences in the temperature required for hydrogenolysis. However it is clear that the benzyl aryl ethers cleave at a lower temperature than do the benzyl alkyl ethers, especially if the latter contain a hydroxyl group. In no case did the benzyl ethers undergo nuclear hydrogenation, *i.e.* the temperature for hydrogenolysis over Raney nickel is lower than for hydrogenation. In some cases where the hydrogenolysis was carried out at 150° or more, the products of that reaction underwent hydrogenation.

It should be pointed out that while Raney nickel has numerous advantages over reduced nickel deposited on a support, the latter is a much better catalyst for the hydrogenation of an aryl ether to the corresponding cyclohexyl compound. The greater tendency of Raney nickel as contrasted with nickel on kieselguhr to cause the rupture of oxygen to carbon linkages was evidenced by the superiority of the latter to bring about nuclear hydrogenation of ethers readily cleared by the Raney nickel.

A precise comparison of the activity of the Raney catalyst with the supported catalyst is impossible not only because they may show their optimum activity for a given compound in quite different temperature ranges but because there is no ratio of catalyst to hydrogen acceptor which would be/

be fair to both catalysts. The ratio of surface to weight of nickel is much higher for the supported than for the Raney catalyst so that comparisons of activities on the basis of weight of nickel are unfavourable to the Raney nickel.

The outstanding characteristic of Raney nickel is its activity at low temperatures and pressures and in the case of all the compounds examined by Adkins, hydrogenolysis proceeded to completion at pressures and (or) temperatures below those at which the supported catalyst was sufficiently active for the satisfactory hydrogenolysis of these compounds, except when the cyclohexyl derivative was required (Covert and Adkins, J. Amer. Chem. Soc., 1932, 54, 4117).

The conditions likely to be necessary for the reduction of this compound were not known, but were estimated roughly by an examination of the temperatures and pressures used by Adkins in his work on the hydrogenolysis of various ethers over Raney nickel. Dibenzyl ether was not among the ethers decomposed by this method, but in the hydrogenolysis of benzyl phenyl ether, 15 minutes at a temperature of 100° and pressure of 150 atmospheres sufficed for the complete decomposition of this ether to toluene and phenol with the formation of only a small amount of cyclohexanol. The diaryl ethers were somewhat more stable, cleavage occurring in the temperature range 150-200°; thus diphenyl ether required 5 hours at 175° for hydrogenolysis, and the high temperature necessary for this decomposition caused the hydrogenation of the products of that reaction.

If the product from the reaction of dibenzyl ether and sulphuric acid has an ethereal structure, it is possible that/

that this structure is symmetrical. and the compound would then be a diaryl ether. As a result, hydrogenolysis at a pressure of 150 atmospheres with a temperature of 150° was performed.

## PREPARATION OF RANEY NICKEL CATALYST.

This catalyst, first prepared by Murray Raney, is available commercially and is prepared by alloying equal parts of nickel and aluminium, and dissolving out the latter with aqueous sodium hydroxide. The commercial catalyst is suspended in water and is satisfactory for many purposes, but a more active catalyst is obtained by the following procedure described by Covert and Adkins (J. Amer. Chem. Soc. 1932, 54, 4116).

Three hundred grams of finely ground nickel-aluminium alloy was added slowly (two or three hours) to a solution of 300 gm. of sodium hydroxide in 1200 mls. of water, cooled in ice. The mixture was then heated on a sand-bath for four hours at 115-120°. A further 400 mls. of a 20% solution of sodium hydroxide was added, and the mixture kept at 115-120° for about 3 hours or until bubbles of hydrogen were no longer evolved, after which it was diluted to a volume of three litres. The clear solution of sodium aluminate was decanted, and the nickel washed by decantation several times and then alternately by suspension and filtration until the filtrate was neutral to litmus. The nickel was then washed with ethyl alcohol and kept under alcohol in a tightly-stoppered bottle.

In a later article on this preparation (J. Amer. Chem. Soc. 1935, 57, 147) Covert and Adkins recommend that the volume of water should be maintained by addition during the reaction of the aluminium with sodium hydroxide, and that the temperature should be lowered to 110° during the period of heating. Raney catalyst prepared by this process is extremely reactive and care must be taken during the washing of/

of the nickel that it does not become too dry, as it will cause spontaneous combustion of the filter-paper on exposure to the air for a short time.

The nickel-aluminium alloy, used in this preparation was made in the Metallurgy Department of the Royal Technical College, and thanks are due to Professor Hay for the facilities granted during the preparation and subsequent grinding of this alloy.

## REDUCTION EXPERIMENTS IN HIGH-PRESSURE AUTOCLAVE.

The attempted hydrogenolysis of this product was carried out in the experimental autoclave in the Technical Chemistry Department of the Royal Technical College and acknowledgment must be made to Dr. W.M. Cumming, Young Professor of Technical Chemistry, both for the facilities offered in the use of plant and equipment in that department and for the helpful advice and information given regarding high-pressure technique.

The autoclave body is of high-tensile steel, tested to a pressure of 6000 $lb/in.^2$ and fitted with a Monel metal liner. The lid of the autoclave body contained a special high-pressure gland through which passed an electrically driven stirrer. The autoclave was heated electrically, and the rate of heating could be followed in various parts of the steel bomb and also within the autoclave liner by means of a series of thermocouples. The autoclave was supplied with twin pressure guages which could be read from behind a blast-screen.

The product from the reaction of dibenzyl ether and sulphuric acid was purified by treating the solution in dioxan with Norite, and drying under vacuum over concentrated sulphuric acid. The Raney nickel was prepared and preserved as previously described.

Since the Raney nickel was so reactive, precautions had to be taken to protect it as much as possible during the transference from the storage bottle to the autoclave. A small amount of nickel, suspended in ethyl alcohol by shaking was quickly poured off from the bulk of the catalyst, mixed with the purified product and the excess alcohol/

alcohol poured off. This mixture was then transferred to the autoclave, which had been previously filled with nitrogen. The presence of a small amount of occluded alcohol has no serious effect on the hydrogenolysis, since the products of hydrogenation of this alcohol are gaseous. Also, nitrogen was used in preference to hydrogen on account of its greater density, and its consequent lower rate of diffusion.

The efficient agitation of the reaction product presented a problem since the electric stirrer fitted in the autoclave was too large to deal effectively with the relatively small quantity of the reaction product which it was possible to use. This quantity of product was governed by the capacity of the autoclave, and since it was unlikely that any of the products of reaction would be gaseous, the amount of substance taken had to be kept small to prevent a large reduction of pressure due to the adsorption of hydrogen in the reaction. From the capacity of the autoclave, it was calculated that the weight of substance should not exceed 20 gms, with an initial pressure of 150 atmospheres. The first method of agitation which was used, consisted in filling the mixture of Raney nickel and the product into small flat tubes, which were fastened by wire to the blades of the stirrer. It was hoped by this means to keep the mixture agitated by the swirling action of the molten substance at the high temperature of the experiment.

<u>EXPERIMENT</u> <u>I</u>. - The initial experiment with the autoclave was carried out using 20 gms. of purified product and 3 gms. of Raney nickel. When the autoclave lid had been fastened in position, hydrogen was blown through the apparatus to free it from nitrogen, the outlet valve closed and the autoclave body filled to a pressure of 110 atmospheres. Heating was slow, and when the temperature had risen to 150° after 3 hours, the pressure was 140 atmospheres. The pressure in/

in the autoclave did not alter for 2 hours after which time it was concluded that no reduction was taking place since no adsorption of hydrogen has occurred.

This inability to bring about hydrogenolysis may have been due to several factors, (1) the use of too low a temperature and pressure and (2) the unsatisfactory nature of the agitation in the autoclave and the consequent inability of the Raney catalyst to act effectively. A further experiment was therefore contemplated in which the maximum conditions used by Adkins in his hydrogenolysis experiments would be employed, i.e. a temperature of $200^{o}$ and a pressure of 200 atmospheres.

The problem of the efficient agitation of small quantities within the autoclave body was mainly one of a structural nature, and it was finally decided to use a solvent to dilute the reaction mixture. For this purpose, several saturated hydrocarbons were examined, and decalin was chosen due to its greater solvent properties and also as its boiling point was close to the maximum temperature which would be used, thus obviating any danger which may have arisen due to liquid pressure. Before use, the decalin was washed with sulphuric acid and caustic soda in order to free the solvent from any unsaturated constituents.

A fresh supply of Raney nickel which was prepared for this experiment was preserved under ethylene glycol. This liquid was chosen in place of ethyl alcohol since the conditions of hydrogenation of this substance have been studied on this autoclave, and it was known that decomposition took place to give only the gaseous products carbon monoxide and methane. (W.M. Cumming, Professor of Technical Chemistry. Private communication). Under the conditions which would be employed in/

in this experiment, the hydrogenation of ethylene glycol would not be excessive. In addition, the gland on the stirrer was lubricated with ethylene glycol, and although it was working against the high internal pressure of the autoclave, leakage of this lubricant into the Monel liner, by capillary action and surface tension always took place. Thus the use of ethylene glycol as a medium for protecting the Raney catalyst did not materially increase the amount of extraneous matter present.

<u>EXPERIMENT</u> <u>II</u>. 15 gms. Purified Product.
100 ml. Decalin
3 gms. Raney nickel (in ethylene glycol).

In this experiment the precautions used previously to protect the catalyst during the addition to the autoclave were not necessary as the nickel was covered either with the ethylene glycol from the storage bottle or with decalin in the autoclave liner.

The autoclave cover was bolted down securely and hydrogen allowed to enter the bomb to the full pressure of a hydrogen cylinder, i.e. 120 atmospheres or 1850 lb/ins.$^2$ and after it was seen that there was no leakage, the stirrer and the heater were switched on.

Observations of the temperature and pressure were made every half hour during the course of the heating up to 150°, and afterwards readings were taken at intervals of a quarter of an hour.

P = Pressure in Autoclave in lbs/in.$^2$

T.A. = Temperature in Autoclave.

t = Time.

T.H. = Temperature in Heater.

| t. | P. | T.A. | T.H. |
|---|---|---|---|
| 1.0 | 2100 | 158 | 238 |
| 1.30 | 2150 | 182 | 258 |
| 2.00 | 2210 | 191 | 254 |
| 2.15 | 2240 | 196 | 262 |
| 2.30 | 2250 | 208 | 270 |
| 3.0 | 2260 | 216 | 269 |
| 3.30 | 2280 | 219 | 270 |
| 4.0 | 2300 | 220 | 267 |
| 4.30 | 2280 | 220 | 265 |
| 4.45 | 2275 | 220 | 265 |
| 5.0 | 2260 | 220 | 263 |

The working conditions in the autoclave were maintained for 2 hours, which is well above the average time required for similar experiments by Adkins, and then the heater was switched off, and the plant allowed to cool overnight. The gas remaining in the autoclave was blown down to a gas-holder.

From an examination of the readings of temperature and pressure, it will be seen that a maximum of 2300 lb./ins.$^2$ (160 atmospheres) had been reached for a temperature of 220°, the pressure began to fall slowly. Previously there had been a marked increase in pressure without any corresponding increase in temperature. This could be explained by the hydrogenation of some of ethylene glycol from the stirrer gland, with the formation of a considerable volume of gaseous products. This was confirmed by taking a sample of gas from the holder and analysing it in a gas-analysis unit. The presence of carbon monoxide and methane was clearly shown, and it is unlikely that these gases could have been formed other than by the hydrogenation of ethylene glycol.

When the autoclave was opened after it had been allowed/

allowed to cool thoroughly, more decalin was added to dissolve the oily product which had separated on the bottom of the liner, and it was seen that two fractions had formed. These were separated, and it was found that one of the fractions consisted of ethylene glycol which had leaked into the liner from the gland. Pure ethylene glycol and decalin are completely mixible and this separation into two layers must have been caused by the presence of water in the ethylene glycol which had been repeatedly used in hydrogenation experiments with this autoclave.

The Raney nickel was filtered off from the decalin solution and the two fractions were distilled separately. The ethylene glycol contained very little dissolved material, while the decalin was very dark and had to be purified first with "Norite". When the volume of decalin had been reduced to about 20 mls., it was allowed to cool and an oil separated out. This liquid was redissolved in dioxan, and after repeated purification with Norite, a solid product was obtained which melted over the range 85-90°. A mixed melting point with this material and the original substance showed no appreciable lowering of the melting range, and this would indicate that the starting material had been returned unchanged. Yield of unchanged substance = 14 gms.

On evaporating the decalin residues a small amount of insoluble product was obtained. Purification of this oily compound was attempted in dioxan, but a solid product could not be isolated even on cooling in ice. Distillation was tried but above 250°, decomposition took place rapidly and no further purification was possible.

These experiments in the high-pressure autoclave have confirmed the experience of the reactions by purely chemical/

chemical methods, that the removal by reduction of the oxygen atom which is believed to present in the reaction product of benzyl alcohol and dibenzyl ether with sulphuric acid only takes place with great difficulty. The conditions under which this hydrogenolysis was attempted, were more vigorous than those which had been found necessary by Adkins and Duzee in a serious of similar experiments (see page 145) and this failure to bring about cleavage of the product would appear to rule out the possibility of its possessing an ethereal structure.

# TREATMENT OF REACTION PRODUCT FROM DIBENZYL ETHER AND SULPHURIC ACID WITH GRIGNARD REAGENT.

In the determination of the structure of the compound obtained by the action of dibenzyl ether and sulphuric acid, it was important to find out the nature of the linkage which bound the oxygen atom in the molecule. The experiments on the hydrogenolysis of this product (see page 143) have shown that it was apparently not an ether, since there was no cleavage of the molecule even under the most rigorous conditions of temperature and pressure. Previous work has also shown (see page 43 ) that the usual tests for a hydroxyl group, such as acetylation and benzoylation, have given only results of a negative nature. There remains, however, the method of Zerewitinoff (Ber., 1901, 40, 2023) who used a Grignard reagent for the estimation of hydroxyl groups.

The basis of this method is the determination of the amount of methane evolved when dry ethereal solutions of the hydroxyl compound and magnesium methyl iodide are mixed, and the reaction proceeds according to the following equation:-

$$R.OH + CH_3\,Mg.I \;=\; R.OMg.I \;+\; CH_4$$

The reaction product, however, is practically insoluble in diethyl ether, but Hibbert and Sudborough (J.C.S., 1904, 85, 933) have modified the process by working in a solution of amyl ether. This solvent, besides having a lower vapour pressure, dissolves the product slightly in the cold, and more easily on heating.

(a) Preparation of Grignard Reagent.

Amyl ether was boiled for some time with sodium, then left over phosphorus pentoxide and finally distilled (B.P. 172-173). A crystal of iodine was added to a mixture of 100 gms. dry amyl ether, 6 gms. magnesium and 35.5 gms. methyl iodide in a R.B. flask. If the reaction did not begin spontaneously/

spontaneously, the mixture was warmed gently, and finally heated on a water-bath for 1 to 2 hours, under reflux and protecting from atmospheric moisture. Any excess of methyl iodide was distilled off in a water-bath and the clear solution decanted into a well stoppered bottle and kept in a desiccator.

(b) Estimation of Hydroxyl Group.

0.5 gms. of the dry substance were introduced into a stout glass flask of 200 c.c. capacity, fitted with a rubber bung which can be connected to a nitrometer filled with dry mercury. Dry amyl ether was added and the substance dissolved by heating. About 15 ml. of the amyl ether solution of the magnesium methyl iodide were placed in a separate tube which was introduced into the flask. The latter was then placed in a constant temperature bath, the rubber bung introduced and connected with the nitrometer. After the bottle has attained the temperature of the bath, the two solutions were mixed by tilting the flask and the mixture thoroughly shaken. When no more gas was evolved the volume, temperature and pressure of the gas in the burette was noted, and from this the weight of methane evolved can be calculated, and since 16 gms. of methane are equivalent to 17 gms. hydroxyl, the percentage of hydroxyl can be determined.

In these estimations it was necessary to vary the conditions in order to find the optimum temperature for the reaction, and this temperature was controlled chiefly by the solubility of the reaction product in amyl ether. The lowest temperature at which 100 ml. of amyl ether would dissolve 0.5 gm. of product was 50°C, but when this temperature was used in the initial experiments, only a small volume of methane was evolved. On examining the mixture, however, it was/

was found that part of the reaction product had been precipitated, probably on the addition of the Grignard reagent. As a result, the temperature was increased to 80°C, and under this condition, both constituents remained in solution.

A blank determination was carried out using 100 ml. amyl ether and 15 ml. Grignard reagent, and when this mixture was heated for 30 minutes at 80°C, 5.5 mls. of gas were collected. An estimation under these conditions was tried and from 0.5 gm. of the reaction product, 25.8 ml. methane were evolved, which is equivalent to a hydroxyl content of 3.61%.

When the time of the action was raised to 45 minutes, a larger volume of methane was collected, but above this limit there was no further increase in the quantity of gas obtained. With this longer time there was a corresponding increase in the blank determination which now gave 6.3 ml. of gas.

### Estimation of Hydroxyl.

100 mls. Amyl Ether.
15 ml. Grignard Reagent.
Time - 45 minutes.
Temperature - 80°C
Blank - 6.3 mls.

| | I. | II. |
|---|---|---|
| Weight of Substance | 0.4893 gm. | 0.4978 gm. |
| Volume of Methane Collected | 32.8 ml. | 33.5 |
| Corrected Volume | 26.5 | 27.2 |
| %age Hydroxyl | 3.87 | 3.94 |

The/

The empirical formula which has already been put forward for this reaction product is $C_{28}H_{26}O$, i.e. $C_6H_5CH_2(C_6H_4CH_2)_3$ OH, and this formula would have a hydroxyl content of 4.45%. Although the experimental results only bear an approximation to this value, they are sufficiently close to indicate the presence of one hydroxyl group in each $C_{28}$ unit.

In an endeavour to obtain results which were in closer agreement with the theoretical value, the estimation was tried using dioxan in which the reaction product was more soluble than in other solvents. This method, however, was not practicable since the dioxan and magnesium methyl iodide reacted to give an additive compound, which was stable even on long exposure to the atmosphere. The only other solvent, in which this estimation could be attempted was dimethylaniline, but as the solubility of the substance therein was less than in amyl ether, this method was not investigated.

# CONCLUSIONS ON THE NATURE OF THE PRODUCT FORMED BY THE ACTION OF BENZYL ALCOHOL AND DIBENZYL ETHER WITH SULPHURIC ACID.

## CONCLUSIONS ON THE NATURE OF THE PRODUCT FORMED BY THE ACTION OF BENZYL ALCOHOL AND DIBENZYL ETHER AND SULPHURIC ACID.

From this study of the reaction of aryl alcohols with sulphuric acid, sufficient information has been obtained to enable the author to arrive at some conclusions regarding the nature of the products. In some cases the work which has been carried out has afforded only results of a negative character, but in general these results have been of interest since they limited both the number and nature of the products which may be formed.

Most of the information from which structural formulae for these compounds may be deduced, was obtained from the first section of the work which describes the reaction of sulphuric acid with several aryl alcohols, and while it must be realised that the preparation of the product from benzyl alcohol and sulphuric acid by synthetic methods through p-benzylbenzyl alcohol, has not given any positive results, these experiments have shown the difficulties which arise in the preparation of an alcohol of this type. At this stage of the work, however, the theory underlying this synthesis, presupposed the existence of an ethereal oxygen atom in the structure, but this was finally disproved by the hydrogenolysis experiments (see page 143) and the treatment of the product with the Grignard reagent, magnesium methyl iodide. (See page 156). As a result, it is necessary that a rearranged structural formula should be devised for this compound on the basis of the data from these experiments.

The formation of complex hydrocarbon derivatives from benzyl chloride in the presence of aluminium chloride (see page 14 ), is analogous to the reaction which is at present/

present being investigated. These hydrocarbon complexes are of two types, a soluble product which has the group $C_6H_5CH_2$ as the structural unit, and an insoluble and infusible substance whose properties can only be explained by assuming a "three-dimensional structure as in the case of Bakelite c" (Jacobsen, J. Amer. Chem. Soc., 1932, 54, 1513).

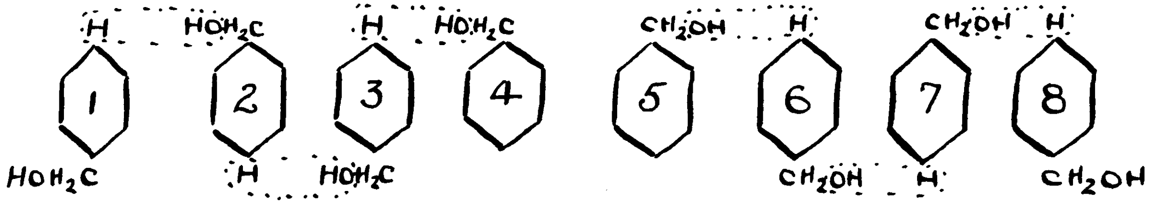
Since none of the products of the reaction of sulphuric acid with aryl alcohols is insoluble or infusible, this would seem to preclude the possibility that they might possess a "three-dimensional" structure, and leaves the alternative theory that they consist of hydrocarbon chains containing the benzyl group as the structural unit. Unlike the condensation of benzyl chloride by the elimination of hydrochloric acid, the reaction of benzyl alcohol with sulphuric acid does not result directly in the formation of a hydrocarbon, but gives a compound which has been shown by analysis still to contain oxygen.

From the estimations with the Grignard reagent, magnesium methyl iodide in amyl ether, it would appear that the product $C_{56}H_{52}O_2$ obtained from benzyl alcohol and dibenzyl ether contains two hydroxyl groups, although the experimental values were low when compared with those required by theory (See page 158). In the absence of Scission by the normal chemical methods of oxidation and reduction, the possibility of this compound containing an ether linkage was examined by hydrogenolysis in the presence of Raney nickel. Such a linkage would have been destroyed under the conditions employed in this experiment (see page 148), but it was found that the product could be recovered unchanged.

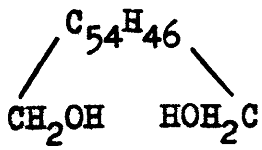
An examination of the possible formula which may be devised for the product from benzyl alcohol, shows that the/

the hydroxyl groups which have been proved to be present are attached to the ends of the chain. The empirical formula $C_{28}H_{26}O$, given by the analysis of this compound requires that there should be one hydroxyl for every four benzyl groups, i.e., $C_6H_5CH_2(C_6H_4CH_2)_3OH$ , but the average value of the molecular weight indicates that the molecular formula is twice this empirical formula and would therefore contain two hydroxyl groups. $HO(C_6H_4CH_2)_8OH$

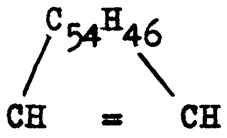
This molecular formula with the hydroxyl groups at the ends of the chain cannot be formulated without involving a reversal in the order of the phenyl and methylene linkages, and it is difficult to see how such a reversal could take place accompanied by chain formation.



Thus if the benzyl groups in this scheme are numbered consecutively from 1 to 8, it will be seen that there is no available linkage between 4 and 5. Also when the formulation of a hydrocarbon such as was obtained by the action of alumina, is attempted using this molecular formula, it is found that the resulting compound would be unsaturated whereas no evidence of unsaturation could be obtained experimentally.



$$\overset{C_{54}H_{46}}{CH_2OH \quad HOH_2C}$$



$$\overset{C_{54}H_{46}}{CH = CH}$$

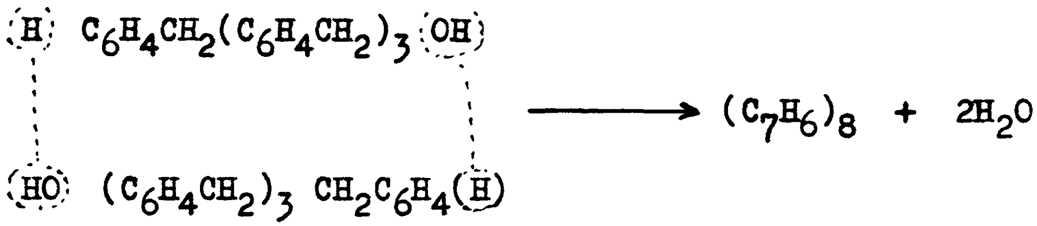
Bogert's work on the cyclo-dehydration of phenylated alcohols (see page 20 ) has proved that the first stage in the/

the dehydration of these alcohols is the formation of an olefine, and then rearrangement of the latter by cyclization, but the formation of the hydrocarbon $(C_7H_6)_x$ in such a manner appears unlikely.

The theory which has been put forward previously, that the values obtained in the molecular weight determination by Rast's method (see page 39 ) were a measure of the degree of association of the compound $C_{28}H_{26}O$, is in accord with the fact that association in solution takes place readily with substances containing a hydroxyl group. These values moreover showed fluctuations which, considering the mechanism of the reaction, are not unexpected, for it is probable that, in addition to the $C_{28}$ units, this compound will contain a small fraction of material in which the number of benzyl groups varies. In a compound with such a high carbon content, such a fraction is difficult to detect by analysis, and this would explain both the variable analyses obtained and the fact that the substance always melted over a range of a few degrees. However, it would appear that the product from benzyl alcohol and sulphuric acid consists chiefly of a compound of molecular formula $C_{28}H_{26}O$, and with a molecular weight of 378.

Using the structure which has already been put forward for the formula $C_{28}H_{26}O$, it is possible to formulate the production of a hydrocarbon which is completely saturated. This could take place by the elimination of the elements of water by means of the hydroxyl group at the end of the chain and a hydrogen atom from one of the benzene nuclei. The analyses of this hydrocarbon indicates that it had the formula $(C_7H_6)x$ where x was of the order 8-10 (see page 54 ), and as it is improbable that association would take place in this case, these results indicate that at least two $C_{28}$ units are/

are involved in the dehydration:- e.g.



$$\begin{array}{l} H\ C_6H_4CH_2(C_6H_4CH_2)_3\ OH \\ HO\ (C_6H_4CH_2)_3\ CH_2C_6H_4\ H \end{array} \longrightarrow (C_7H_6)_8 + 2H_2O$$

This is however, only one of the structures which may be formulated for the hydrocarbon $(C_7H_6)_8$, depending on the positions in the benzene nuclei from which the hydrogen atoms are eliminated. The formation of isomers in such a way might account for the different melting-ranges which were obtained for the fraction which passed through alumina in benzene solution, and the fraction which was recovered from that adsorbent by extraction (see page 53 ).

So far, in constructing this theory, no reference has been made to the fact that this reaction product from benzyl alcohol can also be obtained by the action of sulphuric acid on dibenzyl ether. This can be explained in either of the following ways:-

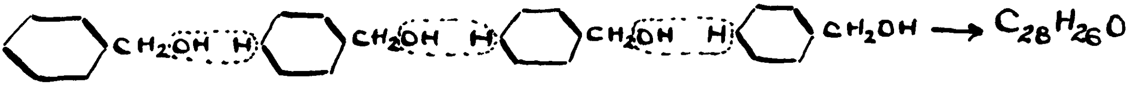
(i) The chief reaction in the formation of this product can be regarded as taking place between sulphuric acid and dibenzyl ether. When benzyl alcohol was used, it would be converted to that ether by the action of the sulphuric acid.

$$4\ C_6H_5CH_2OH \xrightarrow{-2H_2O} 2\ C_6H_5CH_2O\ CH_2C_6H_5 \xrightarrow{-H_2O} C_{28}H_{26}O$$

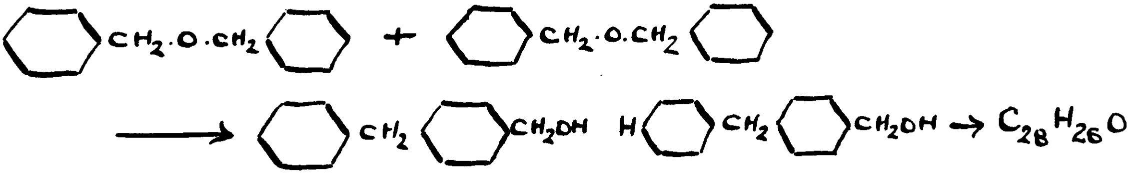
According to this mechanism, however, the product must contain the oxygen atom in the form of an ether linkage and this is not in agreement with the structural formula which has been evolved for this compound.

(ii)/

(ii) Benzyl alcohol may be looked upon as the chief reaction constituent, and the formation of the product from dibenzyl ether can be formulated by means of the rearrangement of dibenzyl ether in the presence of the rearranging agent, sulphuric acid. This method of formation agrees with the experimental facts, the desired hydroxyl group can be formulated at the end of the hydrocarbon chain, and the presence of an ethereal oxygen atom in the structure can be avoided:-



By the rearrangement of two molecules of dibenzyl ether and their subsequent condensation in the presence of sulphuric acid, the formation of the compound $C_{28}H_{26}O$ can also be formulated thus:-



Support for this theory is obtained from the work which has been carried out recently on the rearrangement of benzyl aryl ethers (see page 22 ). The earlier theories which were put forward to explain this action assumed that it only took place in the presence of a rearranging agent, but Belhagel and Freiensehner (Ber., 1934, 67, 1368) have shown that the reaction takes place by heating the ether in the absence of any "foreign" material, but that it is catalysed by a rearranging agent. Sulphuric acid was among other reagents used for this purpose, and in a few cases the action could be controlled by dilution with glacial acetic acid.

There/

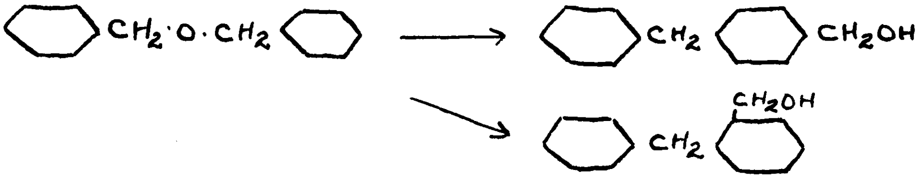
There are no references in the literature to the rearrangement of dibenzyl ether, and the only mention of any similar reaction was to the treatment of this ether with metallic sodium which gave various decomposition products (see page 22). The ether most closely analogous to dibenzyl ether which has been rearranged is phenyl benzyl ether, from which 4 hydroxydiphenylmethane was obtained. (Van Alphen. Rec. trav. chim., 1927, 46, 799).

$$C_6H_5CH_2\,O.\,C_6H_5 \longrightarrow C_6H_5CH_2C_6H_4\,OH$$

The most probable theory for this action is that put forward by Belhagel and Freiensehner who concluded that these rearrangements are brought about by the migration of the benzyl group,[1] which may be intramolecular or to another molecule. These authors consider that the rearranging agent acts simply as a catalyst and does not enter into the reaction. This theory has been extended by Hickinbottom (Nature 1938, 142, 830) who states that these observations find a satisfactory explanation if the assumption be made that the preliminary phase in the rearrangement is the elimination of the migrating group as a free radical. In this assumption Hickinbottom is supported by the fact that the existence of free benzyl radical has been proved by Paneth (J.C.S., 1935, 380), although it was isolated under conditions differing widely from those prevailing in these experiments; such evidence, however, is valuable in that it shows that the theory of scission of benzyl ethers is not without experimental foundation.

By means of this theory, a rearrangement similar to that with phenyl benzyl ether can be formulated with dibenzyl ether, and the formation of the same product from benzyl alcohol and dibenzyl ether can be explained. This mechanism also takes account of the fact that tin linkages may take place/

place in the positions ortho as well as para to the methylene linkages, although previous experimental work by various authors (see page 25) has shown that "para" migration is most usual.



That no such rearrangement has been found to take place experimentally (see page 24) could be explained by the fact that it would require a strong rearranging agent, like sulphuric acid, to bring it about, also as the product from the rearrangement of the ether would contain a free hydroxyl group, it is improbable that it would be obtained unchanged from a reaction mixture containing sulphuric acid.

These theories which have been advanced for the reaction of benzyl alcohol and dibenzyl ether with sulphuric acid can be extended to the substituted aryl alcohols, since they have been shown to form compounds analogous to those obtained from the simple alcohol and ether. In these reactions the positions in the benzene nucleus through which the elimination of water took place were governed by the nature of the substituent groups in the molecule except in the case of p-nitrobenzyl alcohol, when it was found that the presence of the nitro group in the para position to the alcoholic group, inhibited the condensation and dehydration of this alcohol.

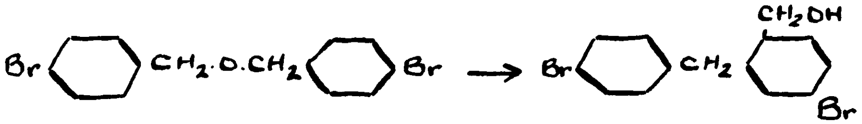
Mention must be made of the special case of p-tolyl carbinol, which gave both the normal reaction product, and also the hydrocarbon formed by the complete elimination of the elements of water from this compound:-

$$4 \text{ X } CH_3C_6H_4CH_2OH \xrightarrow{-3H_2O} C_{32}H_{34}O$$

$$\xrightarrow{-H_2O} (C_8H_8)_4$$

This has already been explained (see page 69 ) on the theory that the presence of the methyl group in the product $C_{32}H_{34}O$, facilitates the ring closure by which the resulting hydrocarbon alone can be formed without causing unsaturation of the molecule. This reaction of p-tolyl carbinol was the only case in which the hydrocarbon, produced by the complete elimination of the elements of water, was obtained by the action of sulphuric acid, no further treatment with alumina being necessary.

The mechanism by which the reaction can take place with dibenzyl ether as well as with benzyl alcohol can be extended to the substituted aryl ethers, since the rearrangement of substituted benzyl phenyl ethers has been carried out by Belhagel and Freiensehner. These authors found that the position in the benzene nucleus to which migration took place was controlled by the directing influence of the substituent groups. The positions which were so influenced, are identical with those through which the elimination of the elements of water occurred in the mechanism described for the reaction of the corresponding substituted alcohols, e.g. in the case of di (p-bromobenzyl) ether, the benzyl group would migrate to the position ortho to the ethereal linkage with perhaps an occasional meta linkage.



This is in accordance with the theory already discussed for the reaction of p-bromobenzyl alcohol and sulphuric acid (page 60 ) and from this it will be seen that identical products can be obtained from these two condensations.

Similar schemes of reaction can be drawn up for the other/

other substituted benzyl alcohols which were treated with sulphuric acid, and in each case the production of the same compound from the aryl alcohol as from its ether analogue, can be formulated by this mechanism.

From the investigation which was carried out by the author, (W.G.C.) the product obtained by Wagner Jauregg and Griesshaber from dibenzyl ether and phosphorus pentoxide, would appear to be of a similar nature to that formed with sulphuric acid. It was, however, more easily soluble in the usual range of organic solvents, and had a higher melting-range than the product formed in sulphuric acid, but did not give the same compound after purification from dioxan and ethyl alcohol. Treatment with alumina gave a hydrocarbon to which these authors assigned the formula $(C_7H_7)_x$. As has already been explained, it is difficult to see how the production of such a compound could be formulated from dibenzyl ether. It is more probable that the correct formula for the hydrocarbon is $(C_7H_6)_x$, as this structure could be obtained by the removal of the elements of water from dibenzyl ether.

$$\frac{x}{2}(C_6H_5\ CH_2)_2O \quad - \quad \frac{x}{2}\ H_2O \quad = \quad (C_7H_6)_x$$

This reaction of dibenzyl ether with phosphorus pentoxide would appear to be similar to the condensation and dehydration of that substance in the presence of sulphuric acid, but as there is no record of the use of phosphorus pentoxide as a rearranging agent, it cannot necessarily be explained by the same theory as was used in the case of sulphuric acid.