THE CATALYTIC HYDROGENATION OF DIPHENYL TRIKETONE.

by

WILLIAM A.P. BLACK, B.Sc.

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CONTENTS.

INTRODUCTION.

In catalytic hydrogenation, the present day worker is faced with a wealth of literature natural to a subject, which, at the beginning of this century gave such an impetus to research in organic chemistry, and which today is of such great industrial importance. A comprehensive review of this literature is impossible here, consequently reference will only be made to some of the more prominent investigations.

Fundamentally the method has remained unchanged from the start, but many different catalysts have been employed. It is chiefly with changes in the nature of the catalyst that this review deals.

The discovery that hydrogen in the presence of suitable catalysts could be used as a reducing agent, introduced a clean straight-forward method capable of exact regulation and wide application.

In general, two methods of hydrogenation are practicable:-

(A) The vapour of the substance together with hydrogen is led over the heated catalyst.

(B)/

(B) The unsaturated body in liquid or dissolved state containing the finely divided catalyst is agitated in an atmosphere of hydrogen.

The reducing power of hydrogen has been known since the early part of the nineteenth century. The hydrogenation of acetylene to ethane (De Wilde, Ber., 1874, 7, 353) was discovered in 1874, and the reduction of substances such as nitrobenzene, in the presence of palladium black had been investigated a few years previous.

It was not until 1897, however, that any systematic study of its application was made. In that year Sabatier in conjunction, first with Senderens, and later with other collaborators, began the work on direct hydrogenation by finely divided metals, which won for him the Nobel Prize in 1912. By a systematic application of the principle to the most diverse organic materials, employing various metals as catalytic agents, he made clear the wide applicability of this method of reduction, accomplishing with success more than two hundred different hydrogenations. The procedure consisted essentially in passing a mixture of the vapour of the substance to be reduced with excess hydrogen through a tube containing the finely divided catalytic agent maintained at a controllable temperature, the products of the

reaction/

reaction being suitably collected on emergence from the heated tube. A detailed account of these reductions is given in his book "La Catalyse en Chimie Organique" (1913).

In 1907 Ipatiev carried out the first hydrogenation under pressure (Jour. Russ. Phy. Chem. Soc., 1907, 39, 381).

In the presence of catalysts such as copper oxide and nickel oxide, using a pressure of two hundred atmospheres and a temperature of 350-400°, he succeeded in reducing a wide variety of compounds, including aromatic aldehydes, ketones, diketones, alcohols, aliphatic compounds with ethylenic linkages, and various terpenes (Ber., 1908, 41, 991; ibid., 1909, 42, 2009, 2092; ibid., 1910, 43, 3546; ibid., 1913, 46, 3589).

Although the use of platinum as a catalyst had been known for some time previously, it was not until 1908 that its possibilities were fully realised. In that year three main methods were worked out.

I. Method of Paal using colloidal platinum as a catalyst. (Ber., 1908, 41, 2733; ibid., 1909, 42, 1541, 1553; ibid., 1912, 45, 2221; ibid., 1915, 48, 287, 994).

II. Method of Skita using colloidal platinum with gum arabic as protective agent (Ber., 1908, 41, 2938; ibid., 1909, 42, 1627; ibid., 1912, 45, 3579).

III./

III. Method of Willstätter using platinum black as catalyst. (Ber., 1908, 41, 1475 to 1918, 51, 767).

To Paal and Skita we owe our present day knowledge of the catalytic action of the colloidal metals of the platinum group, and to Willstätter, the almost general application of palladium and platinum black to direct hydrogenation.

A colloidal catalyst although somewhat more active and more readily prepared is limited in use, as it can only be employed in water, aqueous alcohol or aqueous acetic acid solutions. On the other hand platinum is very convenient, as any solvent can be used, and the product isolated by filtering off the catalyst.

The early investigators found that when platinum black was employed as catalyst, the activity depended on the amount of oxygen absorbed. Euler in 1900, observed that platinum black, which had been freed from oxygen was inactive as a catalyst. The form of this absorbed oxygen then became a question of great interest. In 1916 Wöhler (Jour. Amer. Chem. Soc., 1916, 36, 3475) showed that true oxides or hydroxides were formed when platinum black absorbed oxygen. The subject was later examined by Willstätter and Waldschmidt-Leitz (Ber., 1921, 54, 103) who believed that/

that oxygen played the part of a promoter. They found that oxygen - free platinum, and platinum containing oxygen, behaved like two different substances in reduction processes, and that the toxic action of platinum poisons could be overcome by the admission of oxygen or by increasing the amount of catalyst.

It followed therefore that the oxides of platinum if prepared in a finely divided state would be very effective catalysts. All the oxides of platinum described in the literature were then studied as catalysts, and in 1922 Voorhees and Adams (J.A.C.S., 1922, <u>44</u>, 1397) by fusing a mixture of chloroplatinic acid with sodium nitrate, obtained a very active catalyst, the preparation and properties of which were described in a later paper (Adams and Shriner, (J.A.C.S., 1923, <u>45</u>, 2171). This catalyst, besides being easily prepared, and less sensitive to poisons than platinum black, permits of the reduction of comparatively large quantities of material with relatively small amounts of catalyst, in a short time, at room temperature, and under a pressure of 2-3 atmospheres.

The discovery (Adams and Carothers, J.A.C.S., 1923, <u>45</u>, 1071) that the oxide from recovered chloroplatinic acid was more active than the oxide from which the recovered chloroplatinic acid had been formed/

formed, led to an analysis of the chloroplatinic acid, and the detection of a small percentage of iron. Subsequently, addition of four parts per million of iron in the form of ferrous or ferric chloride was found to accelerate greatly the rate of many reductions. Previous to this, very few examples of promoter action had been deduced.

Quite independently of Adams, Faillebin (Compt. rend., 1922, 175, 1077) carried out concurrently an investigation on the effect of foreign substances on platinum catalysts in the hydrogenation of aldehydes and ketones. By the addition of a suitable promoter a number of aldehydes, which were not reducible under normal conditions, were then reduced. (Carothers and Adams, J.A.C.S., 1925, 47, 1047); Faillebin, Compt. rend., 1926, 182, 138). With many unsaturated aldehydes it was even practicable to reduce the aldehyde group completely before the olefinic linkage was attacked, although other methods caused the reduction of the olefin to take place first.

The success of this catalyst as compared with other forms of catalytic platinum led to a great advancement in the methods of hydrogenation. Many compounds, which previously could only be reduced at high temperatures and pressures could now be satisfactorily reduced under conditions conveniently attained in the laboratory, namely low temperature and pressure.

In/

In 1929 Buck and Jenkins (J.A.C.S., 1929, 51, 2163) in order to obtain certain derivations of α-diketones, investigated the catalytic reduction of the benzils. Previous to this, benzil and benzoin had been reduced by Sabatier and Mailhe (J.A.C.S.Abs., 1909, 3, 1274) at 220-230°with a nickel catalyst and dibenzyl obtained. The method of Adams (Org. Syn., 1928, 8, 10) was chosen and the apparatus modified to deal with quantities of ·005-·01 mole. Benzil was found to reduce readily to benzoin and hydrobenzoin, an almost pure product being obtained after one recrystallisation. In the case of anisil the complete series of reduction derivatives down to p-dimethoxy-diphenyl-ethane was produced catalytically in excellent yield.

The following year, the above investigators, joined by Bigelow (J.A.C.S., 1930, 52, 4495), extended their work to the unsymmetrical α-diketone p-dimethylamino-benzil. The results obtained were the same as in the earlier work, the benzil taking up either one or two molecules of hydrogen to give in the one case the corresponding benzoin and in the other case the hydrobenzoin. The work was continued by Jenkins (J.A.C.S., 1931, 53, 3115) who then studied the reduction products of p-dimethylamino-p-chlorobenzil, and by Buck and Ide (J.A.C.S., 1931, 53, 3510), who investigated the maximal catalytic reduction/

reduction of several mixed benzoins and benzoin itself.

Today, catalytic hydrogenation has penetrated into many of our great chemical industries. The majority of the reductions, however, are carried out at high temperature and pressure, in the presence of a cheap metal catalyst. In 1930, therefore, Adkins (with Connor and Cramer, J.A.C.S., 1930, 52, 4349) began a systematic investigation into the use of nickel as a catalyst. In a bomb made of chrome-vanadium steel, reductions were carried out at pressures of 200-300 atmospheres and temperatures of 200-300°.

Nickel is inferior to platinum as a catalyst in hydrogenations because it is not active at room temperature, but it has the advantage of permitting selective reduction between two reducible groups through control of the temperature of hydrogenation.

Up to this time nickel had been the only base metal catalyst which offered much promise for the hydrogenation of pure organic compounds in the liquid phase, although several oxides and mixtures of oxides had been used. In studying these oxides, Adkins and Connor (J.A.C.S., 1931, 53, 1091) found that a combination of copper and chromium oxides was in many respects superior to any catalyst hitherto known. By means of this catalyst numerous aldehydes, ketones, and esters were quantitatively and rapidly reduced to the/

the corresponding alcohols (Adkins and Connor, loc. cit.; Adkins and Folkers, J.A.C.S., 1931, 53, 1095; ibid., 1932, 54, 1145; Adkins, Wojcik and Covert, ibid., 1933, 55, 1669).

Another very efficient catalyst used by the above investigators was Raney nickel. This is a pure nickel catalyst prepared by alloying equal parts of nickel and aluminium, and dissolving out the latter with aqueous sodium hydroxide. The outstanding characteristic of the Raney catalyst is its activity at low temperatures and pressures. It was found to be an excellent catalyst for the saturation of the c = c linkage in a side chain or in an aromatic nucleus. The copper-chromium oxide catalyst, on the other hand, was rather inactive towards the saturation of an aromatic nucleus, but was very effective at low temperatures for the hydrogenation of multiple linkages in the side chain without affecting the nucleus (Burdick and Adkins, J.A.C.S., 1934, 56, 438).

Hydrogenolysis, which is the cleavage of C to O or C to C bonds accompanied by the addition of hydrogen, has been observed several times to occur as the result of the action of hydrogen in the presence of a catalyst.

Adkins and Connor (J.A.C.S., 1932, 54, 4678) found that the copper-chromium oxide catalyst was very/

very efficient for the hydrogenolysis of oxygenated organic compounds.

Diketones in dry ether with Raney nickel as catalyst were later submitted to the action of hydrogen at 150-200 atmospheres (Sprague and Adkins, J.A.C.S., 1934, 56, 2669). Hydrogenations at 50-125° converted these 1:3-diketones into a variety of compounds depending on the duration of hydrogenation. In most cases the glycol corresponding to the diketone was obtained in good yield. Certain diketones, however, underwent cleavage at either a C to O or a C to C linkage, the hydrogenolysis of the carbon chain occurring with the formation of aldehydes and ketones under quite mild conditions.

Hydrogenation may precede or follow hydrogenolysis. Duzee and Adkins (J.A.C.S., 1935, 57, 147) found that in the case of ethers, the temperature of hydrogenolysis in the presence of Raney nickel was lower than that required for hydrogenation. It is interesting, however, that although hydrogenation did not occur to any considerable extent, the products of hydrogenolysis were themselves hydrogenated under these conditions.

Recently, various ketones have been reduced by Zelinski, Packendorff, and Leder-Packendorf (Ber., 1933, 66, 872) employing platinised charcoal activated with palladium, and by Hartung and Crossley (J.A.C.S., 1934, 56, 158) by means of palladinised charcoal.

An/

An interesting modification lies in the use of heavy hydrogen for the reductions, and a few simple organic molecules have been reduced in this way with a nickel catalyst (Melville, J.C.S., 1934, 797).

Despite the amount of work which has already been carried out, "Catalytic Hydrogenation", still remains one of the most promising and profitable fields of research.

MECHANISM OF CATALYTIC HYDROGENATION.

Catalytic reactions may be regarded as a special type of ordinary chemical reactions, in which one participant emerges finally in its original chemical state.

There are many differences of opinion as to the part actually played by the catalyst.
The theories fall into two classes:-

I. The Physical Theory explains the phenomenon as due to an increase in concentration of the reacting substances at the surface of the catalyst.

II. The Chemical Theory asserts the effect as due to the continuous formation and decomposition of an unstable intermediate compound.

In 1924, Max Bodenstein (Ann. 1924, 440, 177) postulated the parallelism between hydrogenation and detonating gas analysis. He believed, like Willstätter, that the catalyser was a superoxide of platinum which alternately added and gave up hydrogen. Bennewitz and Günther, (Zeit. Phy. Chem., 1924, III, 257) on the/

the other hand, suggested that the activity of platinum was due to the accumulation of hydrogen ions at the surface of the metal. They conducted experiments from which they concluded that hydrogen in contact with heated platinum was ionised. This theory of "Ionic Catalysis", was later supported by Otto Schmidt (Zeit. Phy. Chem., 1925, 18, 193 and Chem. Review, 1933, 363).

The "Intermediate Compound Theory", which is the one now generally accepted was first supported by Sabatier (Ind. and Eng. Chem., 1926, 18, 1005) and Zelinski (Ber., 1925, 58B, 185).

It is definitely known that all hydrogenation catalysts adsorb hydrogen specifically to form a metal-hydrogen adsorption complex, which subsequently decomposes with evaporation of the previous adsorbed hydrogen molecules. This cyclic and continuous kinetic process of adsorption and desorption is one which actually takes place.

Numerous investigators have shown that the order of the energy of activation of various catalysts is in the same sequence as their maximum differential heats of adsorption of hydrogen, indicating that interaction probably takes place between the metal-hydrogen complex and the unsaturated body.

The hydrogen is therefore activated by adsorption, and/

and the complexes may be locked upon as a source of supply of hydrogen in a very reactive state. The ensuing chemical reaction may not differ in essence from an ordinary chemical reaction, save that at least one of the reactants is in an adsorbed or associated condition.

FACTORS CONTROLLING THE RATE OF REDUCTION.

The rate of reduction of a given compound obviously depends on the activity of the catalyst. The conditions which affect the activity are many, among the more important of which are the temperature, pressure, state of division and method of preparation of catalyst, presence or absence of foreign bodies, including solvents, and various factors such as the rate of stirring or degree of agitation.

(1) Effect of Temperature.

The velocity of hydrogenation is usually doubled by a rise of 10^{o}. In many cases a catalyst is only appreciably active above a certain temperature. This minimum temperature of appreciable activity is a factor which depends on the nature of the catalyst rather than on that of the reaction. One of the many advantages of the platinum oxide catalyst used in this investigation, is that it can be used at room temperature. Gentle heating, however, is sometimes employed in order to facilitate the solution of difficultly/

difficultly soluble substances (Buck and Jenkins, loc. cit.)

(2) Influence of Pressure.

Usually an increase in pressure produces a higher reaction velocity, by reason of an increase in molecular concentration. In many reductions a considerable pressure is necessary for reasonably rapid reaction. The platinum-oxide catalyst, at pressures of 2 - 3 atmospheres, effects the reduction of compounds, which Ipatiev (loc. cit.) was only able to reduce with a nickel catalyst at 200 atmospheres. The direct proportionality between velocity and pressure in these reactions has been established by Maxted (Jour. Soc. Chem. Ind., 1921, 40, 169T) and Armstrong and Hilditch (Proc. Roy. Soc. A., 1921, 100, 240). Increase in pressure by increasing the solubility of the hydrogen in the liquid treated, not only speeds up the rate of hydrogenation, but has even been known to modify the nature of the final product.

(3) State of Division of Catalyst.

Other things being equal, the speed of hydrogenation increases as the size of the particles of the/

the catalyst decreases, and for this reason the introduction of colloidal catalysts by Paal and others has facilitated many reactions which take place too slowly with non-colloidal catalysts.

(4) Influence of Previous History of Catalyst.

The activity of a catalyst depends greatly on the temperature to which the catalyst itself, and even the raw materials from which it is obtained, have been subjected during the process of preparation. Exposure to high temperatures causes sintering and a consequent increase in the size of the individual particles. In the preparation of the platinum-oxide catalyst, Adams has found that the temperature of fusion has a marked effect on the reducibility by hydrogen of the oxide produced, and thus on the activity of the product.

(5) Influence of Solvent.

The choice of a suitable solvent is very important. A considerable change in reaction velocity often accompanies a change in solvent, consequently the solvent may be looked upon as a promoter.

In this respect the beneficial effect of glacial acetic/

acetic acid appears to have been fairly generally observed. Adams, Cohen, and Rees, however (J.A.C.S., 1927, 49, 1093) found that acetic acid was not a preferred solvent using the platinum oxide catalyst. Buck and Jenkins (loc. cit.) on the other hand, found that while alcohol was the best solvent for the reduction of the benzoins, glacial acetic acid was most desirable for the reduction of p- dimethylaminobenzil.

The degree to which hydrogenation proceeds in any given case may also be influenced by choice of solvent. For example, Vavon (Compt. rend., 1912, 155, 286) found that acetone in aqueous solution was reduced to isopropyl alcohol, using hydrogen in the presence of platinum, whereas in ethereal solution reduction to propane took place.

(6) The Effect of Foreign Bodies.

Impurities may act either as promoters or poisons.

(a) Promoter Action.

In many cases the activity of the catalyst is considerably raised by the introduction of small percentages of foreign bodies, and the effect of oxygen, water, etc., is very similar to the phenomenon of promotion.

There/

There are various theories on the function of a promoter. Medsforth (J.C.S., 1923, 123, 1452) believes that it is a purely chemical influence, due to a reaction with the adsorption complex, formed between the catalyst and the compounds of the system. Armstrong and Hilditch (Proc. Roy. Soc. A., 1923, 103, 586) on the other hand regard it as merely physical and due to a mechanical extension of the catalytic surface.

Reference has already been made to one of the most remarkable instances of an effect which appears to be akin to promotion, namely the influence of iron salts on the reduction of aldehydes and ketones.

(b) Inhibition of Catalytic Activity.

The presence of certain impurities may inhibit, either partially or completely, the progress of a reduction. A striking point in connection with poisoning lies in the exceedingly small quantities of foreign bodies which may suffice for the complete suppression of activity.

The high degree of toxicity of various impurities was recognised by Sabatier and Senderens at an early stage. Harbeck and Lunge (Zeit. f. anorg. chem., 1898, 16, 50) showed that carbon monoxide acted inhibitively in the hydrogenation of ethylene. Poisoning/

Poisoning by carbon monoxide has been more recently investigated by Thomson (J. Soc. Chem. Ind., 1920, 13, 36 and J.C.S., 1921, 119, 225).

True poisoning occurs chiefly in systems where the catalyst is a solid. It is occasionally mechanical, i.e. caused by the action of a film of dirt or by the accummulation of a solid deposit, but it is more often pseudo-chemical, arising from the accumulation by adsorption of the poison on the catalytic surface.

In the absence of a poison inactivation may be due to the formation of a thin film of carbon (Zelinski, Ber., 1926, 59B, 156). This has been supported experimentally by passing oxygen over platinum, the activity of which has been diminished by use in a reduction process, when the greater part of the original activity was restored.

* * *

THE POSSIBLE REDUCTION PRODUCTS OF DIPHENYL TRIKETONE.

In the reduction of the carbonyl group two stages are possible:-

(1) The formation of an alcohol

$$—CO— \xrightarrow{H_2} —CHOH—$$

(2) The complete reduction to the hydrocarbon accompanied by the elimination of oxygen in the form of water.

$$—CHOH— \xrightarrow{H_2} —CH_2—$$

The reduction of a ketone by the vapour method leads to the formation of the hydrocarbon. Hydrogenations in solvents usually give the alcohol, although sometimes the hydrocarbon is obtained.

Buck and Ide (loc. cit.), however, found that benzoin in the presence of hydrochloric acid could be reduced beyond the hydrobenzoin stage, the elimination of water taking place under the influence of the acid. In this way seven mixed benzoins, and benzoin itself were reduced to the maximum extent giving α,β - dicyclohexylethane and α,β - dicyclohexylethylene glycol. One fact of significance is that for the reduction/

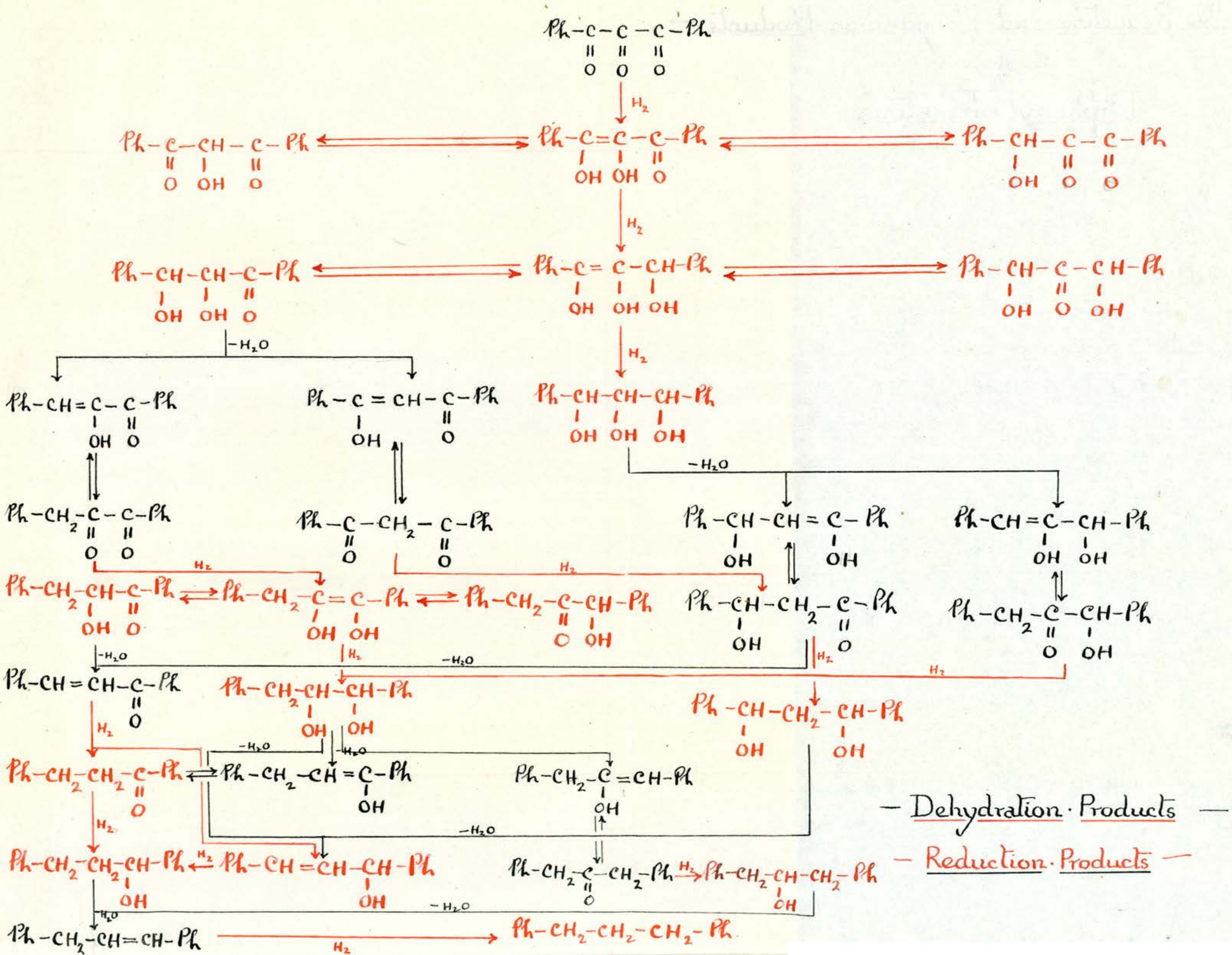
reduction to proceed beyond the hydrobenzoin stage, free hydrochloric acid must be present. In the case of chlorine compounds, this is produced by the action of the hydrogen and the catalyst, the reaction mixture originally neutral becoming strongly acid. It is impossible to fix precisely the mechanism of reduction. The final products are evidently the result of a chain of alternate reductions and reactions involving the elimination of water, during the course of which ample opportunity for polymerization and for side reactions occurs.

Hydrogenolysis, the cleavage of the molecule by the addition of hydrogen, is unlikely under such mild conditions as are used in this investigation.

The catalytic reduction of benzil and its derivatives by Adam's method has been shown by Jenkins, Buck and Bigelow (loc. cit.) to be a simple and effective method of obtaining the numerous reduction products of these 1 - 2 diketones. It seemed, therefore, that this method might be successfully applied to the more complex case of a 1-2-3 triketone, and this investigation describes the first step in the catalytic reduction of the simplest possible aromatic triketone Ph. CO. CO. CO. Ph.

Theoretically the hydrogenation of diphenyl triketone may be imagined to proceed in the following stages. Very few of these reduction products have been previously/

previously described in the literature.



The above scheme does not include the numerous products resulting from the reduction of the benzene nuclei.

previously described in the literature.

Possible · Reduction · and · Dehydration · Products —
— of —
— Diphenyl · Triketone —

The above scheme does not include the numerous products resulting from the reduction of the benzene nuclei.

EXPERIMENTAL.

MATERIALS AND APPARATUS.

Diphenyl Triketone.

The triketone used in this investigation is synthesised from acetophenone.

The acetophenone is first condensed with benzaldehyde to give benzalacetophenone.

$$\mathrm{Ph.\ CO.\ CH_3 + Ph.\ CHO \longrightarrow Ph.\ CO.\ CH{:}\ CH.\ Ph. + H_2O}$$

From the benzalacetophenone, dibenzoyl methane is then prepared by (1) forming the dibromide, (2) methylating the dibromide, and (3) hydrolysing the resulting enolic ether with hydrochloric acid.

$$\mathrm{(1)\quad Ph.\ CO.CH{:}\ CH.Ph + Br_2 \longrightarrow Ph.CO.CH\ Br.CH\ Br.\ Ph}$$

$$\mathrm{(2)\quad Ph.CO.CHBr.\ CHBr\ Ph + 2\,NaOCH_3 \longrightarrow}$$

$$\mathrm{Ph.CO.CH{:}\ C(OCH_3).Ph + 2\ NaBr + CH_3.OH}$$

(3)/

(3) $$\mathrm{Ph.CO.CH{:}C(OCH_3).Ph + H_2O \longrightarrow Ph.CO.CH{:}C(OH)Ph + CH_3OH}$$

$$\mathrm{Ph.CO.CH{:}C(OH)Ph \longleftrightarrow Ph.CO.CH_2CO.Ph.}$$

The dibenzoyl methane after being brominated to the dibromide is then treated with sodium acetate, and the ester obtained hydrolysed to give diphenyl triketone hydrate, which on distillation under diminished pressure gives the triketone.

$$\mathrm{Ph.CO.CH_2CO.Ph + 2Br_2 \rightarrow Ph.CO.C(Br)_2CO.Ph. + 2HBr}$$

$$\mathrm{Ph.CO.C(Br)2\ CO.Ph + 2\ CH_3COONa \longrightarrow Ph.CO.C(CH_3COO)_2CO.PH + 2\ NaBr}$$

$$\mathrm{PH.CO.C(CH_3COO)_2CO.Ph + 2H_2O \rightarrow Ph.CO.C(OH)_2CO.Ph + 2CH_3COOH}$$

$$\mathrm{Ph.CO.C(OH)_2CO.Ph \longrightarrow Ph.CO.CO.CO.Ph + H_2O}$$

PREPARATION OF BENZALACETOPHENONE.

This was prepared according to the method of Kőhler and Chadwell (Org. Syn., 1922, 2, 1). A solution of 109 grams of sodium hydroxide in 980 grams of water and 500 grams of 95% ethyl alcohol was introduced into a beaker fitted with an effective stirrer and surrounded by an ice bath. Into this solution the acetophenone (260 grams) was poured, the stirrer started, and the benzaldehyde (230 grams) added immediately. After 2 - 3 hours stirring, the mixture was placed in an ice box for 20 hours. The yellow solid (463 grams), m.p. 52 - 54°, was washed with water until the washings were neutral to litmus, and finally with 100 cc. ethyl alcohol (cooled to 0°C).

PREPARATION OF BENZALACETOPHENONE DIBROMIDE.

Benzalacetophenone (280 grams, 1 mole) was dissolved in 600 cc of carbon tetrachloride and 160 grams (1 mole) of bromine was added with stirring, according/

according to the instructions of Allen (Org. Syn., 1928, 8, 60). The dibromide (300 grams), m.p. 156 - 157° was filtered off and washed with hot ethyl alcohol.

PREPARATION OF DIBENZOYL METHANE.

This compound was prepared by the method described by Allen (loc. cit.) as follows. A solution of sodium methylate (23.2 grams in 230 cc absolute methyl alcohol) was added with stirring to 184 grams (½ mole) of benzalacetophenone dibromide suspended in 165 cc of absolute methyl alcohol. When the addition was complete, the mixture was boiled under reflux for 3 hours. To the brown liquid was added 140 cc. of water in order to dissolve the sodium bromide. The mixture was then just acidified with hydrochloric acid (Sp. Gr. 1·9) when the colour changed to a light yellow and on oil separated. The acid solution was boiled under reflux for 2 hours and then cooled in ice water with rapid stirring. The solid product (66 grams), m.p. 74-76°, was filtered and washed with alcohol and water. When recrystallised from 95% alcohol/

alcohol (160 cc.) it melted at 76 - 78°.

In connection with this preparation it is interesting to note that the "dibenzoyl methane" was obtained in the enolic form (phenyl α - styryl ketone) which is probably the most stable 1 : 3 - keto-enolic compound known. A considerable amount of work has been done on the tautomeric forms of this compound, but in 1912 Abell (J.C.S., 1912, <u>151</u>, 998) pointed out that the diketonic dibenzoyl methane had never been isolated.

<u>PREPARATION OF DIBENZOYL DIBROMOMETHANE.</u>

Prepared according to the directions of Bigelow and Hanslick (Org. Syn., 1933, <u>13</u>, 58). Dibenzoyl methane (56 grams, 0.25 mole), and 14 cc. of chloroform were placed in a flask equipped with a stirrer, dropping funnel and thermometer, and surrounded by an ice bath. A solution of 25 cc. (0.55 mole) of dry bromine in 230 cc. of chloroform was then added slowly, the hydrobromic acid being continuously removed by aspirating a stream of dry air over the surface/

surface of the solution. The solvent was then completely removed under diminished pressure at room temperature. The solid (75 grams), m.p. 90 - 91° was crystallised from 125 cc. of hot 95% alcohol, after which it melted at 93 - 94°.

PREPARATION OF DIPHENYL TRIKETONE.

A continuation of the synthesis of Bigelow and Hanslick (loc. cit.). Dibenzoyl methane dibromide, (72 grams), was added to a solution of 34.3 grams of fused sodium acetate in 142 cc. of hot glacial acetic acid and boiled under reflux for 2 hours. The mixture was cooled to room temperature and 200 cc. of water added. The white curdy mass (49 grams) was washed well with water, and air dried. This hydrate distilled at 176-178/1-2mm. as a reddish oil, which solidified to a light yellow mass. Recrystallised from 70 cc. ligroin (b.p.100-120°) it separated in light yellow needles (36 grams), m.p. 69° - 70°.

Properties. ~~Beil~~ Ber., 23, 3379; 37, 1531.

PREPARATION OF DIBENZOYL CARBINOL ACETATE.

$$\mathrm{Ph.CO.CH{:}C(OH).Ph + Br_2 \longrightarrow Ph.CO.CH{:}C(OBr).Ph + HBr}$$

$$\mathrm{Ph.CO.CHBr.CO.Ph + CH_3COONa \longrightarrow Ph.CO.CH(CH_3COO).CO.Ph + NaBr}$$

Dibenzoyl bromomethane was prepared by adding 3.6 grams of bromine (1.1 mole) in 10 cc. of chloroform to a solution of 4.5 grams of dibenzoyl methane (1 mole) in 15 cc. chloroform, according to the old method of Neufville and Pechmann (Ber., 1890, 23, 3377). The solvent was completely removed under diminished pressure and the residue (6 grams), m.p. 92.93°, crystallised from alcohol. The bromo compound (5 grams) was boiled under reflux for 1 hour with a solution of 2.5 grams of sodium acetate in 20 cc. of glacial acetic acid. The mixture was then cooled and diluted with water. The white solid, m.p. 94° was recrystallised from methyl alcohol.

PREPARATION OF THE CATALYST.

$$PtCl_4 + 4\ NaNO_3 \longrightarrow Pt(NO_3)4 + 4\ NaCl$$

$$Pt(NO_3)4 \longrightarrow PtO_2 + 4NO_2 + O_2$$

$$PtO_2 + H_2O \longrightarrow PtO_2H_2O$$

Prepared according to the method of Adams, Voorhees and Shriner (Org. Syn., 1928, <u>8</u>, 92) Sodium nitrate, A.R. (18 grams) was added to a solution of 2 grams of alkali-free platinum chloride in 6 cc. of water in a porcelain casserole, and the mixture carefully evaporated to dryness. The temperature was gradually raised, and the full force of the Bunsen burner directed on the casserole for 30 minutes. The mass was allowed to cool and was then treated with 50 cc. of water. The brown oxide (1.2 grams) was washed by decantation, filtered through hardened filter paper on a Gooch crucible, washed until free from nitrates, and dried in a vacuum desiccator.

Properties/

Properties (Adams and Shriner, J.A.C.S., 1923, 45, 2171).

"Exhausted" catalyst was reactivated by dissolving in aqua regia, filtering, evaporating to dryness three times with hydrochloric acid and then with a little water, and finally fusing in the ordinary way with sodium nitrate.

Solvents.

Extra pure B.D.H. benzene; glacial acetic acid; acetic anhydride; absolute and 95% ethyl alcohol, used without further purification.

Hydrogen.

Ordinary commercial hydrogen was found to be quite efficient for the reductions.

THE APPARATUS.

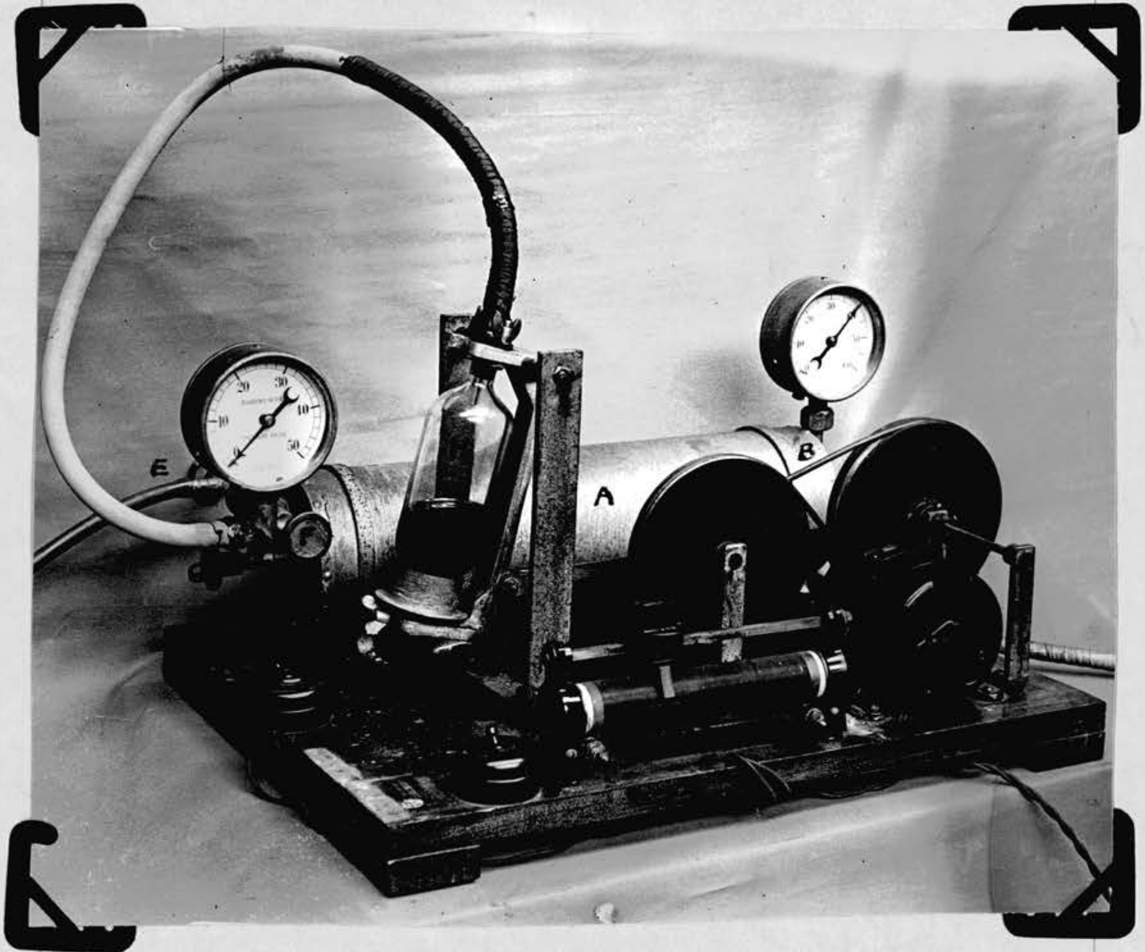


FIG. 1.

The apparatus (fig.1) is similar to that used by Buck and Jenkins (J.A.C.S., 1928, 51, 2163).

A copper cylindrical tank A with openings B and C at either end is used as a container or reservoir for the hydrogen gas. In B is welded a tube holding a Bourdon pressure gauge and a needle valve, through which the reservoir is charged from a cylinder of hydrogen. In C is welded another tube controlled by a needle valve G. Into this tube is welded a third tube K with needle valves E and F at either end. Valve E is used for evacuating the apparatus, and valve F connects to the reaction bottle H, the arrangement being such that the tank A can be shut off from either outlet, and direct connection made between the evacuating pump and the bottle, thus cutting the tank out of the circuit. Between the valve F and the bottle H is a second Bourdon gauge which indicates the pressure inside the bottle.

The connection between the tank and the bottle is made by means of a heavy taped rubber tube, which is connected to a capillary glass tube inserted through the rubber stopper of the bottle.

The reaction bottle, (300 cc. capacity), is of thick pyrex glass, capable of withstanding a pressure of/

of 200 lbs/ □ ". It is held secure in a rocking frame, which is rocked with a variable amplitude by means of a stiff connecting rod and fly wheel, driven by means of a variable speed motor with rheostat. In order to hold the stopper in the bottle when the latter is filled with hydrogen under pressure, a metal strap fixed between the stopper and the rubber tubing is firmly clamped to the top of the rocking frame.

The bottle is heated, when desired, by means of an external electrically heated coil of wire wound inside a cylindrical asbestos shell. A variable resistance in the circuit is used to regulate the temperature.

The whole apparatus is rigidly fixed to a heavy wooden base.

USE OF THE APPARATUS.

In using the apparatus it is essential to guard carefully against leaks and to control the temperature within narrow limits.

The apparatus is first tested for a leak. The reduction bottle is attached to the apparatus, exactly as for a hydrogenation experiment, and is filled with hydrogen to a pressure of two atmospheres. As soon as equilibrium is reached the temperature and pressure are recorded, and the bottle allowed to shake for six hours. If the drop in pressure is less than 0.5 lbs., the apparatus may be considered satisfactory.

The tank A is then filled with hydrogen to a pressure of 4-5 atmospheres. The solution, in a suitable solvent, of the substance to be reduced is poured into the bottle and the catalyst added.

The bottle is attached to the apparatus and evacuated, the valves E and F being open and G closed. Evacuation is continued until the pressure is constant, or in the case of low boiling solvents until the solvent just begins to boil. The valve E is then closed and hydrogen is admitted to the bottle by opening/

opening the valve G. The valve F is closed, and the pressure of the hydrogen in the bottle is read on the gauge. Shaking is commenced, and continued until the theoretical amount of hydrogen has been absorbed. The hydrogen remaining in the bottle is then removed and air is admitted.

The catalyst is recovered by filtering the solution through a hardened filter paper, and the reduction product isolated from the filtrate by distilling off the solvent.

The catalyst is eventually washed with fresh solvent and is then ready for a second reduction.

HYDROGENATIONS.

Temperature and Pressure of Reductions.

The reductions were all carried out at room temperature, 15°, and under a pressure of 2-3 atmospheres, except in the direct reduction of the triketone, where an initial pressure of 5 atmospheres was employed.

Calibration of Apparatus.

A preliminary calibration of the apparatus was carried out for the absorption of one and two proportions of hydrogen, using 0·01 mole of pure benzoin and benzil respectively as standards. Complete hydrogenation to hydrobenzoin corresponded in the first case to a fall of 16 lbs/sq.in. in pressure, and in the second case to 32 lbs/sq.in.

Graphs.

In the majority of the reductions, the hydrogen pressure was plotted against the time, and for the absorption/

absorption of one mole of hydrogen, linear reaction graphs were obtained, characteristic for the hydrogenation of pure substances.

DIBENZOYL CARBINOL FROM DIPHENYL TRIKETONE.

Ph.CO.CHOH.CO.Ph

A solution of 2.38 g. (0.01 mole) diphenyl triketone in 50 cc. pure benzene, containing 0.05 g. catalyst in suspension was placed in the apparatus and hydrogenated until after 1 hour, the pressure had fallen 16 lbs., corresponding to the absorption of 0.01 mole of hydrogen (curve 1, page 58). The catalyst was then filtered off, and the volume of filtrate reduced to 20 cc. by evaporation under diminished pressure at room temperature. Colourless needles separated, 1.45 g., melting at 100-104°. Recrystallisation from 150 cc. ligroin (b.p.80-100°) gave 1.15 g. of long needles, which melted at 110-111.5° to a yellow liquid, the melting point being unaffected by further crystallisation from alcohol. The colourless solid turns yellow at 100°, and if maintained at 106-107° it melts, resolidifies, and again melts to a deep yellow liquid, the complete series of changes occupying about fifteen minutes. The final equilibrium mixture of isomers thus obtained solidifies on cooling and then melts at 96-98°. (Found: C, 75.0; H, 5.1; M.W. in benzene by Menzies Wright Method, (average of four) 238. $C_{15}H_{12}O_3$ requires/

requires C, 75.0; H, 5.0%; M.W.240).

Dibenzoyl carbinol dissolves readily in alcohol and ether, moderately readily in benzene, and more sparingly in ligroin. When shaken in benzene solution with concentrated sulphuric acid, it develops a light orange coloration, as contrasted with the blue colour given by the triketone. An alcoholic solution gives no coloration with ferric chloride, indicating the absence of any appreciable proportion of the enolic form.

The carbinol, 1 g., on treatment with 20 cc. acetyl chloride at 50° for half hour, gave the acetyl derivative (92% yield), separating from methyl alcohol in rhombic plates which melted at 93°, either alone or admixed with an authentic specimen of the acetate prepared according to the method of Neufville and Pechmann (Ber., 1890, <u>23</u>, 2375).

The molecule of the acetate breaks down on attempted hydrolysis, as had already been recorded by the above authors, and they did not succeed in isolating the parent dibenzoyl carbinol.

DIBENZOYL CARBINYL ACETATE FROM DIPHENYL TRIKETONE.

$Ph.CO.CH(OCOCH_3)CO.Ph$

A solution of 2.38 grams of diphenyl triketone in 50 cc. of acetic anhydride, containing 0.05 grams of catalyst was placed in the bottle surrounded by the heater. The solution was heated to 60°, the air removed, and hydrogen admitted. After 13 minutes, when approximately $^4/_5$ mole. of hydrogen had been absorbed, the reduction stopped. After filtering off the catalyst the solution was diluted with an equal volume of water. The white solid which separated weighed 2.5 grams (89% of the theoretical) and melted at 90-91°. When recrystallised from alcohol it melted at 93-94°. A mixed melting point with dibenzoyl carbinyl acetate prepared by the method of Neufville and Pechmann (loc. cit.) showed no depression.

NOTE.- By slightly increasing the amount of catalyst so as to obtain the absorption of exactly one molecule of hydrogen it is quite probable that the yield of the acetate would be 100%.

* * *

α-γ-Diphenyl-glycerol from Dibenzoyl Carbinol.

Ph.CHOH.CHOH.CHOH.Ph

Dibenzoyl carbinol, 2.40 g. (0.01 mole) dissolved in 50 cc. benzene was reduced at room temperature, using 0.10 g. catalyst until after 1 hour two molecular proportions of hydrogen had been absorbed (curve 2, page 62.). The syrup obtained by filtering the hot solution from the catalyst and evaporating off the solvent, crystallised when covered with light petroleum ether and melted at 80-82° (yield, 97% of the theoretical). The crude product dissolved readily in hot benzene (45 cc.) to a highly refracting solution, which deposited colourless needles or prisms. After being dried for several hours at 60°, or maintained in vacuo over calcium chloride for two weeks these gave the anhydrous compound, m.p. 84.5-85°.

(Found: C, 73.8; H, 6.5; Calc. for $C_{15}H_{16}O_3$: C, 73.8; H, 6.5%. M.W. in boiling benzene, (C = 0.4, 0.64) 244, 246. Calc. valve 244).

When the finely divided compound was allowed to stand/

stand overnight in a moist atmosphere it was converted quantitatively into the monohydrate, m.p. 97-99°, also obtainable in large rhombic plates by crystallising the anhydrous form from aqueous (1:1) alcohol.

When a weighed quantity of the monohydrate (3.16 g.) was powdered and dried at 60° for 48 hours the loss in weight was 6.5%. (The theoretical loss corresponding to one mole of water is 6.9%). (Found: C, 68.8; H, 6.9. Calc. for $C_{15}H_{16}O_3H_2O$: C, 68.7; H, 6.9%. M.W. in benzene (C = 0.8) 264. Calc. value 262).

Diphenyl glycerol exhibits a very strong tendency to undergo hydration. If the anhydrous compound is crystallised from a small amount of dry benzene, without filtration, the solution deposits the pure anhydrous product. On filtering small quantities of such a solution through filter paper which has not been specially dried, the deposited crystals are found to be of the hydrated form. In a desiccator over calcium chloride, complete dehydration requires about a fortnight, the melting point of the product passing through a minimum value of 80-81°.

Diphenyl/

Diphenyl glycerol has a sweet taste and is appreciably soluble in water. It dissolves readily in alcohol and ether, is moderately soluble in benzene, and sparingly so in petroleum ether. A benzene solution of the compound shaken with concentrated sulphuric acid gives a characteristic bright red coloration. The solid compound dissolves in sulphuric acid to a brilliant purple solution with a fruity odour; on standing, a precipitate slowly forms, and on the addition of a drop or two of water, the mixture turns white and the smell of benzaldehyde is quite definite.

Diphenyl glycerol (1 g.) was boiled for 30 minutes with 20 cc. of acetic anhydride. On pouring the cooled solution into water 1.4 g. (93% yield) of the triacetate deposited, m.p. 84-85°. The pure derivative separates from aqueous (1:1) alcohol, in plates, m.p. 85-86°. On admixture with diphenyl glycerol (m.p. 85°) the product melted at 67-70°. On hydrolysis with N/2 alcoholic potassium hydroxide, the triacetate regenerates diphenyl glycerol in good yield.

(Found: C, 68.1; H, 5.8; $C_{21}H_{22}O_6$ requires C, 68.1; H, 6.0%

H, 6.0%. M.W. in boiling benzene 361 (average of four). Calc. 370. Hydrolysis gave CH_3CO, 34%: Calc. value, 35%).

On repeating the above hydrogenation with a smaller amount of catalyst (0.075 g.) a deposition of crystalline diphenyl glycerol began as soon as one molecular proportion of hydrogen had been absorbed. This deposit tended to envelop and deactivate the catalyst, with the result that the absorption of the final molecular proportion of hydrogen occupied 3 hours (curve 3, page 63.).

α,γ-DIPHENYL-GLYCEROL FROM DIPHENYL TRIKETONE.

Diphenyl triketone (2.38 g.) dissolved in 50 cc. benzene was converted into diphenyl glycerol in one operation using 0.15 g. catalyst, and an initial pressure of 5 atmospheres (curve 6, page 69.). An almost theoretical yield was obtained.

α,β-DIHYDROXY-γ-KETO-α,γ-DIPHENYL PROPANE OR AN ISOMER THEREOF.

$Ph.CHOH.CHOH.COPh \rightleftarrows Ph.CHOH.CO.CHOH.Ph$

Dibenzoyl carbinol, (2.40 g.), was reduced as above using 0.05 g. catalyst, until after 2 hours 0.01 moles of hydrogen had been absorbed. After filtration, the pale yellow solution was seeded with diphenyl glycerol and allowed to stand overnight, when 0.3 g. of diphenyl glycerol (hydrated form) deposited and was removed. Evaporation of the solvent left a white solid, 1.9 g., m.p. 67-70°, which on being twice recrystallised from ligroin (b.p. 100-120°) gave colourless well formed needles, m.p. 87-89°. As in the case of dibenzoyl carbinol, fusion is accompanied by a colour change to yellow. (Found: C, 74.2; H, 5.9. M.W. in benzene, (average of four) 240. $C_{15}H_{14}O_3$ requires C, 74.4; H, 5.8 per cent. M.W. 242).

The same product m.p. 86-88°, was obtained by reducing 2.38 g. diphenyl triketone, using 0.1 g. of catalyst/

catalyst and 50 cc. benzene until two molar proportions of hydrogen had been absorbed (curve 4, page 65).

The dihydroxy compound strongly depresses the melting points of dibenzoyl carbinol and of diphenyl glycerol. It dissolves in concentrated sulphuric acid to a clear yellow solution, which gradually turns red, and develops a green fluorescence. An alcoholic solution gives no coloration with ferric chloride. The solubility in organic solvents is intermediate between that of the related carbinol and glycerol.

Hydrogenation of the dihydroxy compound (1.21 g.) in benzene (30 cc.) using 0.05 g. catalyst, converted it in 40 minutes (curve 5, page 67) into diphenyl glycerol (1.0 g.). The latter deposited from benzene in rhombic plates of the hydrated form, m.p. 97-98°.

The above hydrogenations were also successfully carried/

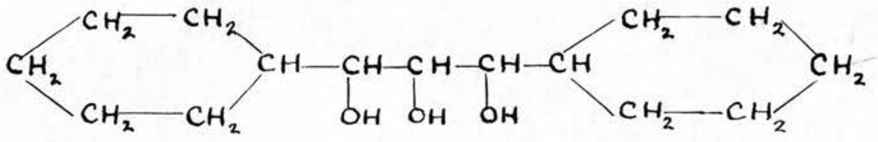
carried out with glacial acetic acid, absolute and 95% alcohol as solvents, and with different amounts of catalyst.

DEHYDRATION OF DIPHENYL GLYCEROL.

Diphenyl Glycerol 2.44 grams (0.01 mole) was heated for twenty minutes with 20 cc. of a mixture of glacial acetic acid and hydrochloric acid (Sp.Gr. 1.19), 4:1 by volume. After adding 200 cc. of water the solution was neutralised with aqueous sodium carbonate when an oil separated.

Similar dehydrations were carried out at temperatures from 60°-100°, but in every case treatment of the acid solution resulted in the formation of a small amount of yellow oil, with a strong smell of benzaldehyde. This was not investigated any further.

α,γ- DICYCLOHEXYL-GLYCEROL FROM DIPHENYL TRIKETONE.



A solution of 2.38 grams (0.01 mole) of diphenyl triketone in 50 cc. of glacial acetic acid, containing 0.30 grams of catalyst, was hydrogenated at 15°. After 2 hours, when 4 moles of hydrogen had been absorbed, the reduction slowed up considerably. The exhausted catalyst was filtered off and 0.20 grams of new catalyst added, when a further molecular proportion of hydrogen was absorbed in 3 hours. After three further additions of 0.20 grams of catalyst, the reduction stopped, the total absorption being between 8-9 moles of hydrogen. The time required for the complete reduction was about 15 hours.

The above procedure was found to be far superior to the method of Buck and Ide (loc. cit.) who in reducing the benzoins added 1.0 gram of catalyst at the beginning, and found that the reduction took several days.

After filtering off the catalyst, the acetic acid solution was diluted with an equal volume of water and the resulting white solid filtered off. It is interesting/

interesting to note that this solid is fatty in nature, rising to the surface of the water like a thick cream. It weighed 1.9 grams (73% of the theoretical), and melted at 131-133°. When recrystallised from benzene it separated in rhombic plates, which melted at 139°. Unlike diphenyl glycerol it does not form a hydrate, the melting point being unaffected on further recrystallisation from aqueous (1:1) alcohol. (Found: C, 70.5; H, 11.0.M.W. in benzene (average of four) 256 $C_{15}H_{28}O_3$ requires C, 70.3; H, 10.9% M.W. 256).

α, γ - Dicyclohexyl-glycerol is slightly soluble in hot water, very soluble in alcohol and ether, moderately so in benzene, and more sparingly in ligroin. It gives a colourless solution with a bright purple fluorescence, when shaken in the solid form, or in benzene solution, with concentrated sulphuric acid, and gives no coloration with alcoholic ferric chloride.

α, γ - Dicyclohexyl-glycerol (1 gram) was boiled for 30 minutes with 30 cc. of acetic anhydride. The cooled solution, when poured into water deposited 1.4 grams (93% yield) of the crude triacetate, m.p. 74.76°./

74-76°. The pure derivative separated from alcohol in thick needles, m.p. 83-84°.

The triacetate is practically unaffected by boiling dilute hydrochloric acid, but concentrated hydrochloric acid causes dehydration, and rupture of the molecule. On hydrolysis with $^N/_2$ alcoholic potassium hydroxide, 0.5 grams of the triacetate gave 0.30 grams (90% yield) of the original glycerol. (Found: C, 66.1; H, 9.1. M.W. in benzene (C = 0.6) 380 $C_{21}H_{34}O_6$ requires C, 66.0; H, 8.9. M.W. 382).

NOTE.-

Buck and Ide (loc. cit.) report that the related compound, α,β - dicyclohexylethylene-glycol, is unaffected by boiling concentrated hydrochloric acid, while the parent hydrobenzoin is readily dehydrated. The glycol formed only a monacetyl derivative, the hydrolysis of which is not recorded.

α, γ - DICYCLOHEXYL-GLYCEROL FROM α, γ - DIPHENYL-GLYCEROL.

Diphenyl glycerol (2.44 grams, 0.01 mole) in 50 cc. of glacial acetic acid was reduced at room temperature, 15°, using 0.20 grams of catalyst, until after 2 hours 2 moles of hydrogen had been absorbed. The exhausted catalyst was filtered off and 0.20 grams of fresh catalyst added, when a further molecular proportion of hydrogen was absorbed. By renewing the catalyst, as soon as the reduction slowed up, the glycerol was made to take up approximately six molecules of hydrogen. The complete reduction took 8-9 hours, and 1.0 grams of catalyst was required. After filtering off the catalyst, the filtrate was treated as in the previous experiment. The yield of dicyclohexyl-glycerol was 2.2 grams (86% of the theoretical). It was obtained pure after one recrystallisation from benzene.

REDUCTION OF DIPHENYL TRIKETONE AT 70°C.

A solution of 2.38 g. of diphenyl triketone in 50 cc. of a mixture of glacial acetic acid and concentrated hydrochloric acid (4:1 by volume), containing 1.0 g. of catalyst was placed in the bottle surrounded by the heater, and heated to 70°. The air was removed, hydrogen admitted, and the shaker started. After $2\frac{1}{2}$ hours when approximately 5 moles of hydrogen had been absorbed, the reduction slowed up. The exhausted catalyst was filtered off and it was noticed that small droplets of oil had separated out from the acid solution. A fresh portion of catalyst (0.5 g.) was added when a further molecular proportion of hydrogen was absorbed in one hour. Reduction beyond this stage was found to be impracticable, the deposited oil causing coagulation of the catalyst. From observations it appears that the amount of catalyst required to bring about complete reduction to the saturated hydrocarbon would actually be in excess of the amount of material reduced. The small amount of oil which separated from the acid solution had a very pleasant smell reminiscent of octyl acetate.

Adam's catalyst is unsatisfactory, therefore, for the complete reduction of the triketone to the hydrocarbon.

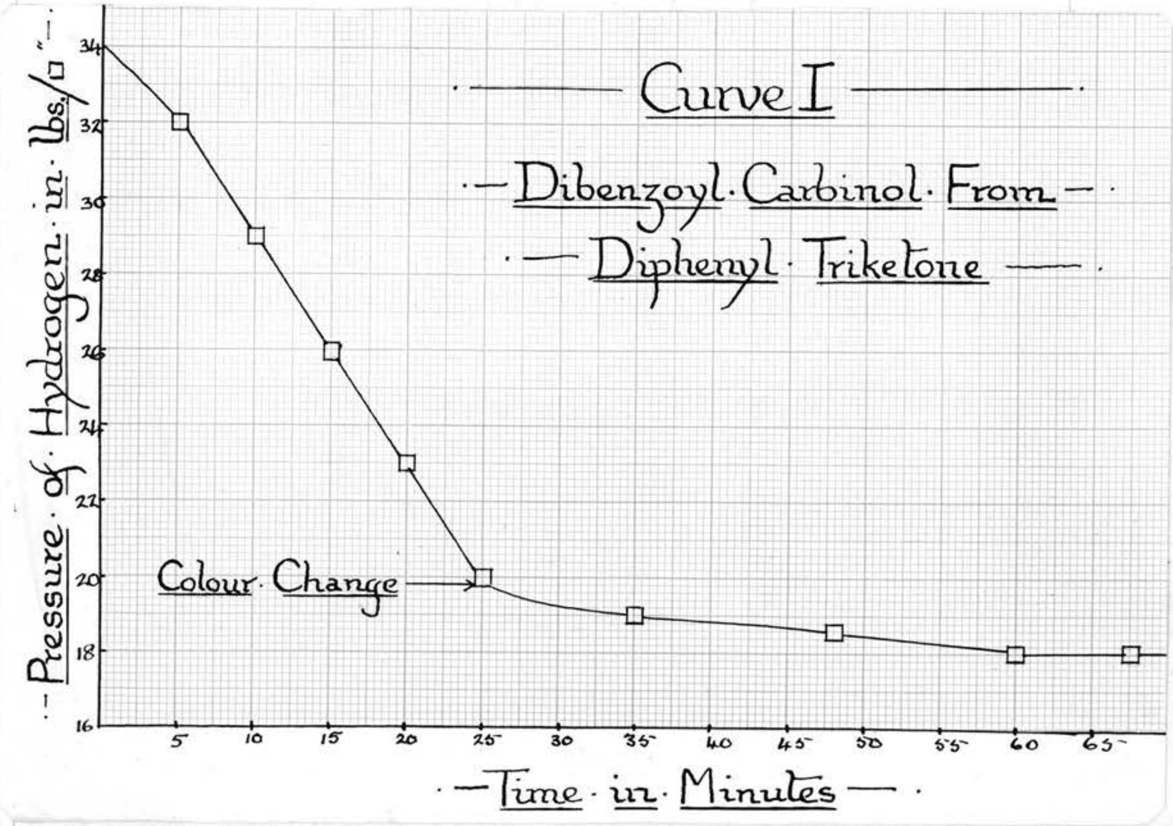
α, β - DICYCLOHEXYLETHYLENE-GLYCOL? FROM HYDROBENZOIN.

The method is a modification of that used by Buck and Ide (J.A.C.S., 1931, 53, 3510). Hydrobenzoin (1.1 g. 0.005 mole) in 50 cc. of glacial acetic acid containing 0.30 grams of catalyst in suspension was hydrogenated at 15°. The first molecular proportion of hydrogen was absorbed in 3 minutes, the second in 7 minutes and the third in 25 minutes after which the reduction slowed up. The exhausted catalyst was filtered off and 0.20 grams of fresh catalyst added, when 3 further molecular proportions of hydrogen were absorbed in 55 minutes. At the point corresponding to the absorption of 5 moles of hydrogen, crystals separated out from the acid solution. The catalyst was filtered from the hot solution, which on cooling deposited 0.9 grams (78% of the theoretical) of white flat prisms m.p. 193°, the melting point being unaffected by further recrystallisation from glacial acetic acid. This compound is no doubt identical with that obtained by Buck and Ide but glacial acetic acid appears to be much more satisfactory for the reduction than the solvent used by these authors, the product being obtained pure without recrystallisation. As the above authors do not quote any yields the methods cannot be compared, but their statement that the presence of free hydrochloric acid is essential for the reduction appears to be unfounded.

SUMMARY AND DISCUSSION.

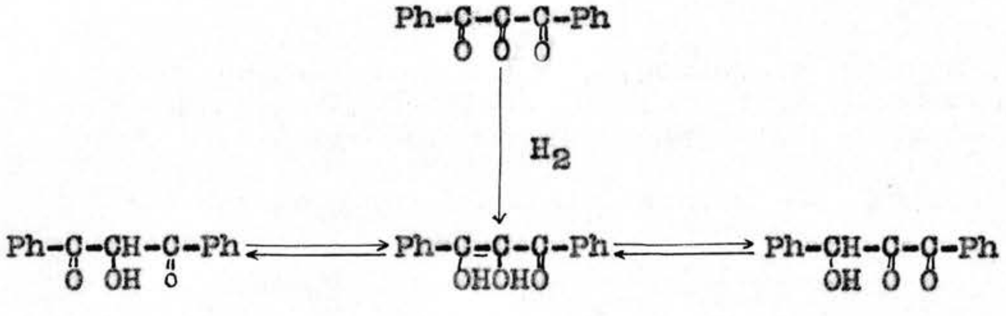
DIBENZOYL CARBINOL.

The present investigation has shown that the reduction of diphenyl triketone by catalytic hydrogenation under pressure can be carried out in stages by adjusting the character and quantity of the catalyst. In the majority of the reductions pure benzene was used as solvent and no experimental difficulties were experienced provided the proper conditions were observed. When 0.05 gm. of catalyst was employed the triketone (0.01 mole) took up one molecule of hydrogen and no more, and was converted into the hitherto unknown dibenzoyl carbinol, thus affording a comparatively ready means of preparing this interesting compound. On plotting the hydrogen absorption against the time a linear reaction graph was obtained which is reproduced below.



Practically no initial "lag" was observed, indicating that the time required for the reduction of the brown inactive platinum-oxide catalyst to the lower active oxide, or to platinum black, was very small. As soon as the shaker had picked up speed, rapid absorption of hydrogen began. When exactly $\frac{7}{8}$ mole of hydrogen had been absorbed, the colour of the solution changed from yellow to green, and the absorption of the remaining $\frac{1}{8}$ mole took place very slowly, after which no further absorption occurred. Curve I was found to be reproducible, provided the same "stock" catalyst was employed.

The absorption of one mole of hydrogen might be expected to lead, as is known to be the case with benzil (J. Thiele, Ann., 1899, <u>306</u>, 142) to the preliminary formation of an unsaturated diol I which would ketolise into dibenzoyl carbinol II or its isomer III.



$$\begin{gathered} Ph-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-Ph \\ \downarrow H_2 \\ Ph-\underset{\overset{\|}{O}}{C}-\underset{OH}{CH}-\underset{\overset{\|}{O}}{C}-Ph \rightleftharpoons Ph-\underset{OH}{C}=\underset{OH}{C}-\underset{\overset{\|}{O}}{C}-Ph \rightleftharpoons Ph-\underset{OH}{CH}-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-Ph \end{gathered}$$

II I III

A/

A reduction of the triketone was therefore carried out in hot acetic anhydride solution in order to try and arrest this dihydroxy compound in the form of the diacetyl derivative. The reduction took only 13 minutes and gave dibenzoyl carbinol acetate in almost theoretical yield. It does not appear, therefore, that the first step in the reduction of the triketone is the formation of the diol I. There remains always the possibility that this diol is actually formed, but is so unstable at 60° that it immediately ketolises into dibenzoyl carbinol.

In diphenyl triketone, however, we have three carbonyl groups, and although the reactivity of the terminal ketone groups will have been suppressed somewhat by the steric hindrance due to the adjacent benzene nuclei, they will still exert an activating influence on the central carbonyl group which will consequently be highly active. These considerations lead to the prediction that the central carbonyl group will exhibit an enhanced activity whereas the terminal ketone groups will show less tendency to participate directly in the reactions of the molecule. In benzil the two ketone groups would have equal activity and would therefore be reduced at the same rate to give the diol. In the triketone, however, the enhanced activity of the central group should lead to the direct/

direct formation of dibenzoyl carbinol, a supposition which seems to be confirmed by experiment.

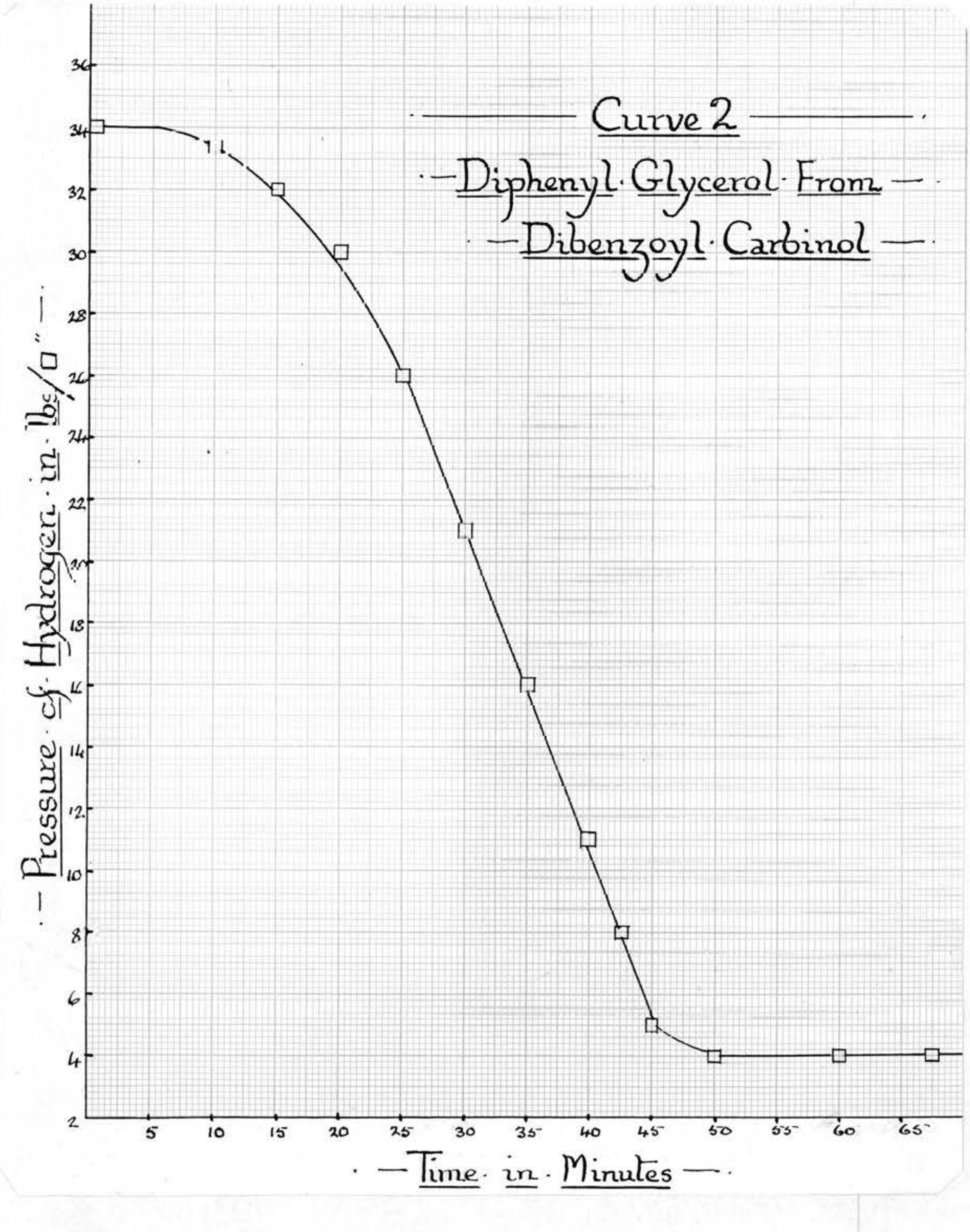
The dibenzoyl carbinol was obtained in excellent yield in the form of long white needles, which on rapid heating melted at 110-111.5°, undergoing a change to pale yellow at 100° without visible melting or shrinking. On being maintained at 106°, however, the pale yellow needles melted, resolidified to a deeper yellow opaque mass, and again melted to a deep yellow liquid, the complete series of changes occupying about 15 minutes.

These changes are interpreted as indicating a tendency for the carbinol to undergo isomerisation. The fact that the white solid turns yellow at 100° may indicate a change to the isomer III (page), which having two carbonyl groups adjacent to each other would undoubtedly be coloured. It is quite possible, therefore, that even on rapid heating, the recorded melting point is not the true melting point but is the melting point of a mixture of the two tautomeric forms.

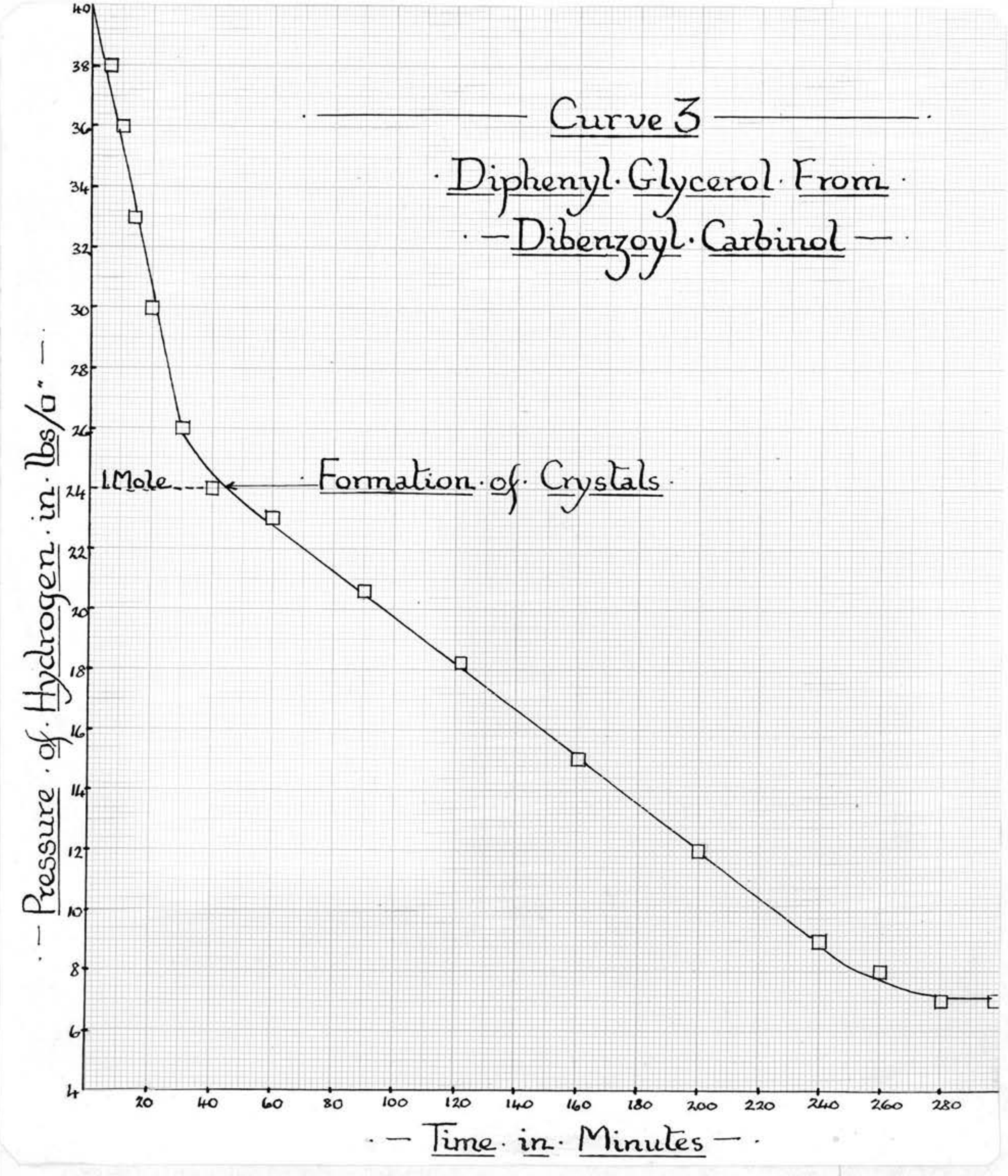
On treatment with acetyl chloride, the carbinol was converted quantitatively into the known acetyl derivative which had previously been prepared by Neufville and Pechmann (loc. cit.)

DIPHENYL GLYCEROL.

Dibenzoyl carbinol readily underwent further hydrogenation. Rapid reduction, using 0.10 grams of catalyst, led without any break in the time pressure curve (curve 2) to the absorption of two molar proportions of hydrogen with the formation of - - diphenyl glycerol. The yield was practically quantitative.



On the other hand, by employing only 0.075 grams of catalyst, a break in the hydrogenation became evident after the absorption of one molar proportion (curve 3), at which point crystals of diphenyl glycerol began to separate.



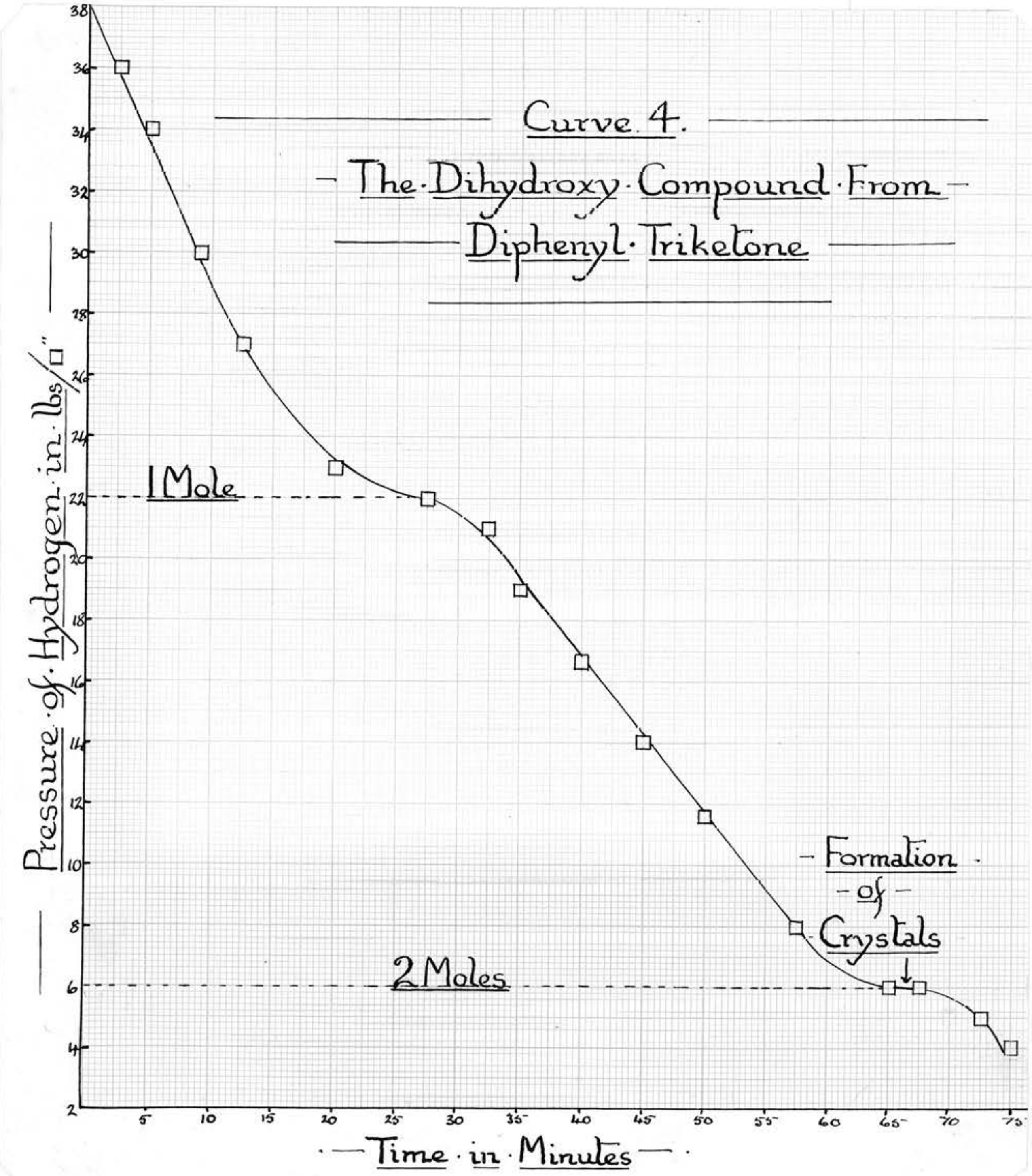
In curve 2 the lag at the beginning was due to the fact that the carbinol was not completely in solution, and also because the suspended compound delayed the reduction by enveloping the catalyst. In curve 3 gentle heating was applied at the beginning to facilitate the solution of the carbinol, with the result that rapid absorption of hydrogen began at once. It is essential, therefore, that for rapid reduction the compound to be reduced, and the products of reduction should all be in solution.

Diphenyl glycerol has a sweet taste, and is appreciably soluble in water. In moist air or aqueous solvents it forms a crystalline monohydrate, m.p. 97°-98°, which loses water comparatively readily in vacuo or at higher temperatures to give the anhydrous product m.p. 85°. Acetylation gives rise to a crystalline triacetate which melts at 85°-86°.

A further point of interest lies in the structural resemblance between this compound and trihydroxyglutaric acid, which exists in two meso and two optically active forms. An attempt to resolve this glycerol by means of l-menthoxy acetyl chloride was unsuccessful, due to the fact that the resulting ester could not be obtained in a crystalline condition.

α, β -DIHYDROXY-γ-KETO-α,γ-DIPHENYL PROPANE.

Starting from either dibenzoyl carbinol or diphenyl triketone (Curve 4), and using a suitable amount of catalyst, a break in the time-pressure curve was noted at the stage corresponding to the formation of the intermediate dihydroxy compound.



Curve 4.

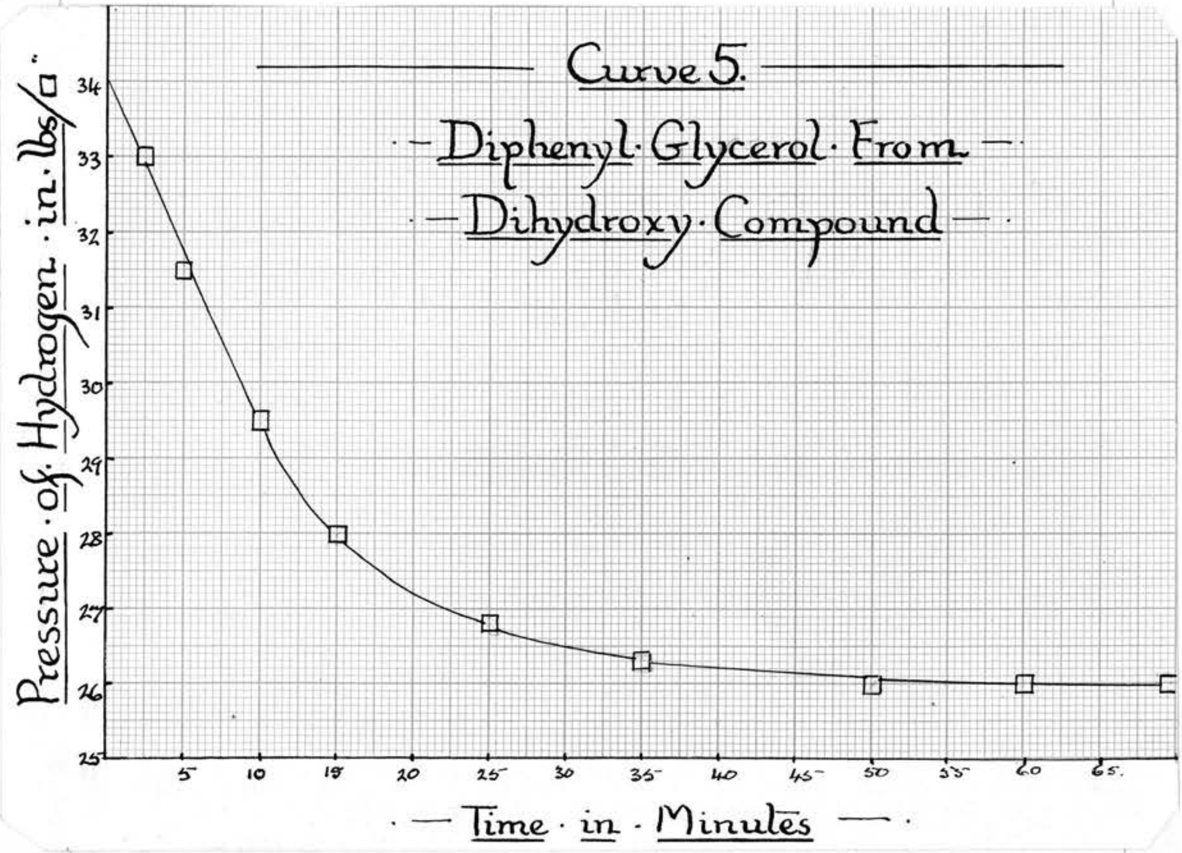
The Dihydroxy Compound From Diphenyl Triketone

On interrupting the reduction at the point corresponding to the dihydroxy compound, the situation was found to be somewhat complex. In this case some diphenyl glycerol was always formed, and since it was by far the least soluble of all the products at all events in organic solvents, it always appeared as an impurity depressing the melting point of the main product and resulting in the formation of more or less intractable oils. However, by suitable manipulation it was found possible to obtain a moderate yield of the dihydroxy compound in colourless needles which exhibited small variations in melting point, 86-89°, according to the rate of heating. This compound readily underwent further hydrogenation to form α,γ-diphenyl-glycerol in good yield (curve 5).

α,γ-DIPHENYL GLYCEROL FROM THE DIHYDROXY DERIVATIVE.

The reduction of the dihydroxy derivative to diphenyl glycerol was considerably slower than that of the triketone or the carbinol, the following curve/

curve being for the reduction of 0.005 mole of substance in the presence of 0.05 grams of catalyst.



Curve 5.

Diphenyl · Glycerol · From

Dihydroxy · Compound

Although the dihydroxy compound was isolated

in/

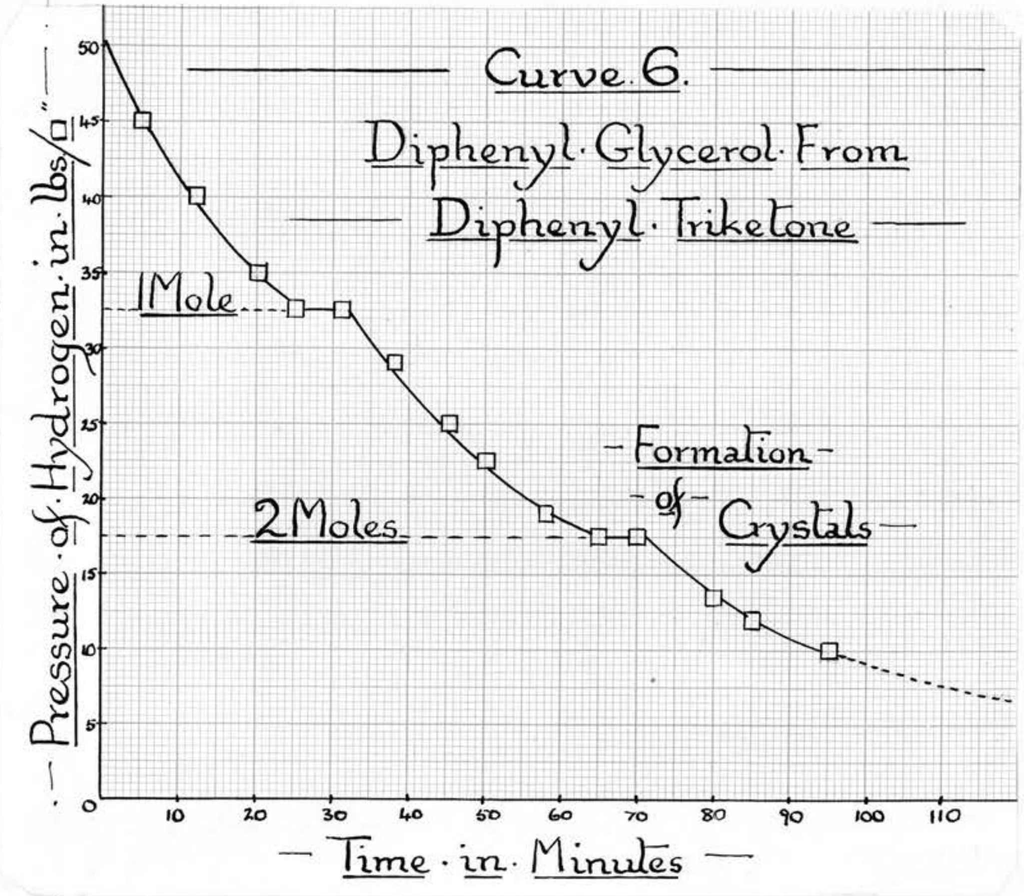
in well formed crystals which depressed the melting point of either the carbinol or the glycerol, and gave good analytical figures, acetylation of the compound only gave rise to an uncrystallisable oil. The variable melting point, and difficulty of isolating any definite acetyl derivative, suggest that this compound readily isomerises on heating or in solution.

In the case of keto-enolic isomerides it has been shown that the extreme mobility of one or both of the forms renders them liable to isomeric change, not only in the presence of a reagent, but frequently by rise of temperature, action of light, or action of a solvent. In this investigation, therefore, no attempt was made to ascertain the structural formula of the dihydroxy compound.

α,γ-DIPHENYL GLYCEROL FROM DIPHENYL TRIKETONE.

When 0.15 grams of catalyst was used the direct reduction of diphenyl triketone to diphenyl glycerol took place without difficulty. The pressure-time curve (curve 6) shows two points of inflection, indicating the successive formation of dibenzoyl carbinol,/

carbinol, the dihydroxy compound and diphenyl glycerol in the solution.



From the curve it can be seen that the first molecular proportion of hydrogen was absorbed in 30 minutes and the second in 40 minutes. The third stage occupied four hours, partly because the reduction of the dihydroxy compound is a slower reaction (page 67) and partly owing to the crystalline deposit of diphenyl glycerol carrying down part of the catalyst; only a portion of the corresponding curve is therefore reproduced in the diagram.

DEHYDRATION OF DIPHENYL GLYCEROL.

Buck, Jenkins and Bigelow (loc. cit.) in reducing the benzoins found that the hydroxylic reduction products readily underwent dehydration when heated with a mixture of glacial acetic acid (4 volumes) and concentrated hydrochloric acid (1 volume). Whereas the substituted hydrobenzoins were dehydrated to give the corresponding desoxy compounds, hydrobenzoin itself gave a mixture of an anhydride and diphenyl acetaldehyde. It was therefore decided to attempt the dehydration of the diphenyl glycerol in the same way, in the hope that a single product would result.

With the hydrobenzoins dehydration simply involves the splitting off of one molecule of water with the formation of a desoxy compound.

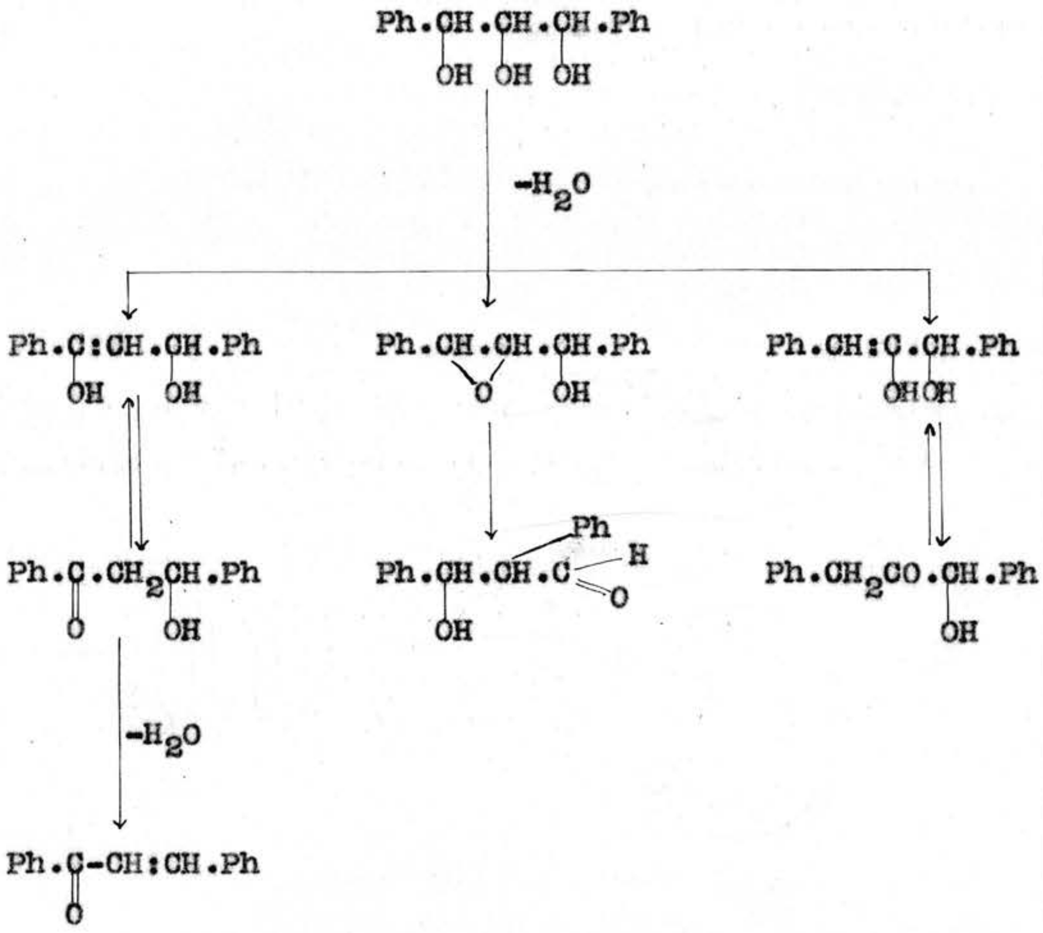
VIZ.-

$$\text{-CHOH.CHOH-} \xrightarrow{-H_2O} \text{-CH}_2\text{CO-}$$

With diphenyl glycerol, however, dehydration is much/

much more complicated, a number of products being theoretically possible.

VIZ.-



Various dehydrations were carried out at temperatures from 60-100°, but in every case subsequent treatment of the acid solution with water gave a small amount of a yellow oil, which had a strong smell of benzaldehyde, indicating that cleavage/

cleavage of the molecule had taken place. The method, therefore, did not seem suitable for the preparation of any one of the dehydration products, and it was not considered advisable to continue this line of investigation at the present stage.

α,γ-DICYCLOHEXYL-GLYCEROL.

In preparing diphenyl glycerol from diphenyl triketone it was found that when the amount of catalyst was increased from 0.15 grams to 0.20 grams the yield of the glycerol was reduced from 90% to 50%. As this could only be due to a reduction of the glycerol, with the formation of a compound more soluble in benzene, it was decided to reduce the triketone to the maximum extent. Reduction of the solvent (benzene) is not impossible here. Willstätter and Hatt (Ber., 1912, 45, 1471), for example, found that one gram of benzene in the presence of 0.6 grams of Loew's platinum black absorbed at room temperature and in seven hours, the theoretical amount of hydrogen required for the formation of hexahydrobenzene. By working in glacial acetic acid, reduction actually took place more quickly and less platinum was required/

required. These considerations, coupled with the fact that in the present case deposition of the glycerol from benzene solution slowed up the reduction considerably, suggested the use of glacial acetic acid as a solvent.

A reduction was therefore carried out under these conditions, employing a temperature of 15° in order to eliminate the possibility of the glycerol being dehydrated. By repeatedly renewing the catalyst, the triketone was completely reduced in 15 hours to give α,γ-dicyclohexyl-glycerol in excellent yield. This compound was also obtained by completely reducing diphenyl glycerol in glacial acetic acid solution at room temperature, the reduction taking 8-9 hours.

α,γ-Dicyclohexyl-glycerol has interesting properties which are partly aliphatic in nature. It was obtained pure after one recrystallisation from benzene, separating in the form of rhombic plates which melted sharply at 139°. It resembles diphenyl glycerol in that it forms a crystalline triacetate, m.p. 83-84°, but differs in that it does not form a hydrate.

As is to be expected, the hydrogenation of the ketonic groups of the intensely coloured triketone molecule, leads to the formation of colourless crystalline products, the solubilities of which in alcohol/

alcohol and water increase progressively as we pass from the hydroxy derivative to the dihydroxy compound and to the glycerol. On the other hand the solubilities decrease in benzene and ligroin. Thus, diphenyl glycerol is more soluble in alcohol but much less soluble in benzene and ligroin than the dihydroxy compound, the carbinol or the triketone, the solubilities being in the above mentioned order. The dicyclohexyl glycerol, on the other hand, is only slightly soluble in hot water, and it is much more soluble in benzene and ligroin and much less soluble in alcohol than the diphenyl glycerol. By reducing the latter compound to dicyclohexyl glycerol, therefore, the direction of the solubility changes has thus been reversed.

COMPARISON BETWEEN THE MAXIMUM REDUCTION OF DIPHENYL TRIKETONE AND THAT OF BENZIL.

It is interesting at this point to compare the reduction with one carried out by Buck and Ide (J.A.C.S., 1931, 53, 3510). By reducing benzoin in a solution of 40 cc. of alcohol and 10 cc. of concentrated hydrochloric acid, they obtained α, β - dicyclohexylethane and a compound melting at 194° which they believed to be α, β -dicyclohexylethylene glycol. They state quite definitely, however, that for reduction to proceed beyond the hydrobenzoin stage free hydrochloric acid must be present. When carried out at 70° they found the reduction took only two hours, while several days were required at room temperature.

In the reduction of the triketone at 15°, as carried out during the present investigation, glacial acetic acid was used as solvent and the hydrogenation to dicyclohexyl glycerol occupied several hours, the amount of catalyst, however, was in excess of that used by the above workers, and was added in small successive amounts instead of in one lot at the beginning.

As far back as 1913, when catalytic hydrogenation was/

was still in its infancy, Sabatier and Murat (Compt. rend., 1913, 156, 1851) discovered that the catalytic reduction of a carbonyl group took place much more easily than the hydrogenation of the benzene nucleus. They found, however, that on hydrogenating the ketone $Ph.CH_2CH_2CO.CH_2CH_2Ph$ by the vapour method, in the presence of not very active nickel at 180° the carbonyl group only was reduced, but similar treatment with very active nickel at 165° gave the corresponding dicyclohexyl hydrocarbon, the benzene nucleus in this case being also attacked.

Although the above case cannot be compared directly to one in a liquid medium, it nevertheless illustrates that complete reduction depends to a great extent on the character of the catalyst.

In the reduction of the triketone, diphenyl glycerol is first formed, followed by reduction of the benzene nuclei. The benzene nucleus appears, therefore, to be much more easily reduced under these conditions than the CHOH group, in fact no case is recorded in the literature where Adam's catalyst has strictly speaking effected the direct reduction of such a group.

The reduction of a substituted benzoin to a substituted diphenylethane, as carried out by Buck and Jenkins (J.A.C.S., 1929, 51, 2163), is the result of/

of alternate reduction and dehydration and not of direct hydrogenation. The benzoin is first reduced to a hydrobenzoin, which readily loses water in the warm acid solution to give a desoxybenzoin:-

$$\text{-CHOH.CO-} \xrightarrow{H_2} \text{-CHOH.CHOH-} \xrightarrow{-H_2O} \text{-CH}_2\text{CO-}$$

The substituted desoxybenzoin is again reduced to a stilbene hydrate, which dehydrates to give a substituted stilbene, which is then reduced to the hydrocarbon:-

$$\text{-CH}_2\text{CO-} \xrightarrow{H_2} \text{-CH}_2\text{CHOH-} \xrightarrow{-H_2O} \text{-CH:CH-} \xrightarrow{H_2} \text{-CH}_2\text{CH}_2\text{-}$$

Hydrobenzoin itself, on the other hand, is known to dehydrate to yield diphenylacetaldehyde and an anhydride, and further reduction and dehydration must take place in order to give the hydrocarbon. It is rather surprising, however, that although hydrobenzoin is easily dehydrated, Buck and Ide (loc. cit.) found that α, β. dicyclohexyl-ethylene glycol was unaffected by boiling concentrated hydrochloric acid. The complete reduction of benzoin, as carried out by Buck and Ide, would thus appear to be a very complicated process. A certain proportion of hydrobenzoin must first be formed and reduced to dicyclohexylethylene glycol/

glycol while the remainder must undergo dehydration. The above workers do not quote any yields or even attempt to explain why the glycol itself does not undergo dehydration and, moreover, they regard the identification of the glycol as provisional only.

Assuming that the reduction is carried out at room temperature, it does not seem likely that dehydration will take place even in the presence of concentrated hydrochloric acid.

In order to bring the mechanism of the benzil reduction into line with that of the triketone, a reduction was carried out at 15° using glacial acetic acid as solvent. Starting with 0.005 mole of hydrobenzoin, complete reduction was found to take place in 90 minutes, giving the compound, m.p. 193°, (α, β-dicyclohexylethylene glycol) in 78% yield. When 5 moles of hydrogen had been absorbed this compound separated out from the acetic acid solution in the form of flat plates and was found to be pure without further crystallisation. The reduction of diphenyl glycerol, on the other hand, was considerably slower, but it gave the α, γ-dicyclohexyl glycerol in 86% yield. The two reductions are thus identical. Starting from benzil or diphenyl triketone, hydrogenation leads first of all to a reduction of the ketonic groups to give carbinol groupings, followed by a reduction of the benzene nuclei.

REDUCTION OF DIPHENYL TRIKETONE IN ACID SOLUTION AT 70°.

A reduction of the triketone was now carried out at 70°, in a solution of glacial acetic acid and concentrated hydrochloric acid, in the hope that complete reduction to the hydrocarbon would take place. Reduction proceeded smoothly until seven molecules of hydrogen had been absorbed. At this point the presence of the hydrocarbon was quite evident and by separating out from the acid solution it caused the coagulation of the catalyst. Addition of new catalyst produced further reduction, but it was obvious that for complete reduction, the amount of catalyst required would be greatly in excess of the amount of material reduced. The small amount of oil obtained, which had a very pleasant odour reminiscent of octyl acetate, was insufficient for identification.

The dehydration and reduction of diphenyl glycerol in hot acid solution was attempted, but could not be carried to completion, possibly on account of the toxic action of one of the intermediate products on the platinum catalyst.

The complete reduction of diphenyl triketone to α, γ -dicyclohexyl propane is exceedingly complex on account of the large number of possible intermediate reduction/

reduction and dehydration products (page 23.). In the hot acid solution there is also the chance of polymerization and numerous side reactions. Such a reduction is unsuited to the method used in this investigation, but could no doubt be readily accomplished by the vapour method.

CONTROLLING FACTORS IN THE REDUCTION OF DIPHENYL TRIKETONE.

The following investigation takes into consideration those influences on the course of hydrogenation specifically connected with the catalyst and the solvent. Consequently all the results described refer to the same temperature and pressure conditions, namely 15^{o} and 2-3 atmospheres, and are for the reduction of 0.01 mole of diphenyl triketone.

(1) The Catalyst.

The reduction products of diphenyl triketone exert a definite toxic action on the platinum oxide catalyst, in fact the phenomenon may be compared to one of "beneficial poisoning" where the reaction is slowed down by the presence of a specific material, in such a way that the catalytic process stops short at an intermediate stage in the sequence of a possible chain of reactions. This toxic action, or gradual poisoning of the catalyst during hydrogenation, was overcome by increasing the amount of catalyst, and by aeration of the exhausted catalyst. The above type of/

of poisoning must be distinguished from another form encountered in this investigation, namely the deposition of crystals in the reduction mixture which exert a deactivating effect on the catalyst by covering up the surface and preventing contact between it and the other interactants.

The reductions tabulated below (table 1) were carried out with the object of determining the rate and extent of hydrogenation as controlled by the concentration of the catalyst. In order to obtain an accurate comparison the reductions were all carried out under carefully standardised conditions, and with a "stock" platinum catalyst possessing constant and known activity. Thus, the catalyst used throughout was old reworked catalyst from the same fusion, and the triketone was from the same distillation. Extra pure benzene (50 cc.) was used as solvent and the impurities could therefore be taken as constant throughout.

TABLE I./

Weight of Catalyst	Times of Absorption of Hydrogen		
	1st Mole	2nd Mole	3rd Mole
0.05 grams	20 mins.	No Absorption	-
0.10 "	10 "	60 mins.	No Absorption
0.15 "	7 "	14 mins.	$\frac{5}{8}$ mole in 4 hours.
0.20 "	5 "	5 "	50 mins.

TABLE I.

From the above table it can be seen that the weight of catalyst controls the extent of hydrogenation and thus determines the products of reduction.

A change in the proportion of catalyst definitely affects the speed, in fact the figures prove that the rate of reduction of diphenyl triketone is directly proportional to the weight of the catalyst, other factors being equal.

This is therefore one of the most interesting cases where a reduction can be carried out in stages simply by adjusting the amount of the catalyst.

The/

The platinum oxide prepared from recovered chloroplatinic acid (obtained by dissolving spent catalyst in aqua regia and converting into the chloride by evaporating several times with hydrochloric acid) was found to be much more active than the oxide from pure platinum chloride. Reductions were carried out in benzene (table 2) and alcohol (table 3) solutions, using new and reworked catalyst, under the same conditions of temperature and pressure.

Catalyst	Times of Absorption of Hydrogen		
	1st Mole	2nd Mole	3rd Mole
0.20 grams "New" Catalyst	15 mins.	15 mins.	120 mins.
0.20 grams "Reworked" Catalyst.	5 "	5 "	50 "

TABLE 2.

Catalyst	Times of Absorption of Hydrogen		
	1st Mole	2nd Mole	3rd Mole
0.20 grams "New" Catalyst	20 mins.	30 mins.	90 mins.
0.20 grams "Reworked" Catalyst	6 "	10 "	30 "

TABLE 3.

This increased activity which has been observed by several investigators was first examined by Adams (J.A.C.S., 1922, 45, 1071) who found that it was due to the presence of a trace of iron which acted as a promoter. The reduction of diphenyl triketone, therefore, appears to be one which can be easily accelerated by the addition of a promoter.

The Solvent.

In all hydrogenations, the selection of a proper solvent is very important. In many reductions, for example, the solvent exerts a specific influence not merely/

merely on the speed but also on the course of the reaction. In this investigation, reductions carried out with different solvents (50 cc.) using 0.20 grams of "stock" catalyst under carefully standardised conditions, show that the reduction of the triketone to dibenzoyl carbinol is very rapid and is independent of the nature of the solvent, whereas reduction of dibenzoyl carbinol to the dihydroxy compound takes place much more easily in benzene than in acetic acid or alcohol (table 4). The reduction of the third carbonyl group is very slow compared to the reduction of the first two, but appears to take place more easily in 95% alcohol than in alcohol or glacial acetic acid.

Solvent	Times of absorption of hydrogen.		
	1st Mole	2nd Mole	3rd Mole
Benzene	5 mins.	5 mins.	50 mins. *
95% Ethyl Alcohol.	6 "	10 "	30 "
Glacial Acetic Acid	6 "	15 "	40 "
Abs. Ethyl Alcohol.	6 "	15 "	50 "

TABLE 4.

* The longest time observed at this stage was due to precipitation of diphenyl glycerol from solution resulting in deactivation of the catalyst.

Although a number of investigators have found that the presence of a trace of water, as in alcohol, inhibits the reduction very markedly, this is not the case with diphenyl triketone despite the fact that the latter compound is exceedingly hygroscopic.

In the preparation of dibenzoyl carbinol benzene was found to be the most satisfactory solvent, bringing about an easy separation of the reduction products. It is also advisable to use benzene in the preparation of diphenyl glycerol, as deposition of the glycerol from solution prevents further hydrogenation. Glacial acetic acid, on the other hand, was found to be the best solvent for the complete reduction of the triketone to α, γ -dicyclohexyl-glycerol.

Effect of Temperature.

Reductions took place very rapidly at 60°, but the higher temperature resulted in a mixture of products. Thus, when diphenyl triketone was allowed to absorb 1 mole of hydrogen at 60°, about 10% of the product was diphenyl glycerol, and very little dibenzoyl carbinol could be recovered from the mixture. The toxic action of the triketone appeared to be more definite at 60° and no advantage was therefore gained in carrying out reductions other than at room temperature.

ATTEMPTED RESOLUTION OF DIPHENYL GLYCEROL.

Diphenyl glycerol like trihydroxy glutaric acid can theoretically exist in two meso and two optically active forms, and it was therefore decided to attempt a resolution of this interesting compound in the hope of determining whether the form obtained on hydrogenation is meso or racemic. Diphenyl glycerol readily forms a crystalline triacetate when heated with acetic anhydride, and it seemed likely, therefore, that it could be combined with an optically active acid chloride and the resulting product, if racemic, could be separated by fractional crystallisation.

Very few optically active acid chlorides are known suitable for this purpose, but l-menthoxyacetyl chloride has recently been used with success by Read and Grubb (J. Soc. Chem. Ind., 1932, 51, 329 T.) for the resolution of dl-menthol, the acid chloride reacting readily with the dl-menthol in pyridine or quinoline solution to give two diastereoisomeric esters, which were easily separated from each other by fractional crystallisation.

The required l-menthoxy acetic acid was prepared according to the method of Frankland and O'Sullivan (J.C.S.,/

(J.C.S., 1911, 99, 2329) as modified by Rule and Tod (J.C.S., 1931, 1932, 1934). Numerous experiments involving varying conditions were carried out with the acid chloride and the glycerol, but no crystalline ester could be obtained. This is not surprising, however, when one considers the number of possibilities. For example, acetylation of the racemic product may give rise to a mixture of the optically active forms of the monacetyl, diacetyl and triacetyl esters, which would almost certainly be isolated as a syrupy liquid. On the other hand if we assume that there is very little steric hindrance due to the terminal phenyl groups of the glycerol, and that a homogeneous triacetyl derivative is formed, the melting point of this derivative would undoubtedly be low.

The syrupy ester obtained from the interaction was therefore fractionated (1) by dissolving it in the minimum amount of benzene and partially precipitating with petroleum ether, or (2) by dissolving it in alcohol and bringing about partial precipitation by careful addition of water. The resulting syrup, however, was still of such a nature as to be unfit for analysis. It is difficult to say, therefore, whether one or more of the hydroxyl groups of the glycerol undergo acetylation, although the yield of crude ester/

ester seems to indicate the formation of a triacetyl. After approximately three quarters of the ester had been removed by the above treatment, the residual oil was hydrolysed and the product purified by steam distillation and crystallisation, when the diphenyl glycerol was recovered in an inactive form, identical to that obtained from the hydrogenation experiments.

On theoretical grounds the diphenyl glycerol should not be easily racemised, but until some other method of resolution has been tried it cannot be definitely stated that the product obtained on hydrogenation is of the meso type.

PREPARATION OF 1-MENTHOXY ACETYL CHLORIDE.

This was prepared, as already stated by the method of Rule and Tod. Menthol (312 grams, 2 mols.) was placed in a distilling flask, the side tube of which was stoppered and the neck fitted to a long air condenser. The flask was heated to 150° in an oil bath, and 12 grams of sodium (½ mole) added in small pieces through the condenser. When all the sodium had/

had dissolved the excess menthol was distilled off under diminished pressure in a current of hydrogen. The sodium menthoxide which remained in the flask was dissolved in 200 cc. of sodium dried benzene, and the solution introduced into a litre round bottom flask. A solution of 20 grams of chloroacetic acid in 200 cc. of dry benzene was then added gradually and the mixture heated in an oil bath (110-115°) for 24 hours. The sodium menthoxy-acetate was washed out with water, the aqueous solution acidified with sulphuric acid and the free menthoxy acetic acid extracted with ether. The ether extract, after being dried, was concentrated to a syrup, and the syrup distilled under diminished pressure. A first fraction gave an acid of $\left[\alpha\right]_D^{17}$ - 95.4°, in ethyl alcohol (C = 2.630). Yield 48 grams, m.p. 32 - 34°. On repeating the process the acid, (36 grams, b.p. 164°/7 mm) had $\left[\alpha\right]_D^{17}$ - 96.2° in ethyl alcohol (C = 3.350, l = 2); and $\left[\alpha\right]_D^{17}$ - 96.6° in methyl alcohol (C = 2.344).

<u>NOTE</u>.-

The rotations observed were all slightly higher than those recorded in the literature,e.g. Read and Grubb, (loc. cit.) quote $\left[\alpha\right]_D^{18}$ - 91.7° (C = 2.1011, l = 2, abs. Et.OH). The l-menthoxy acetyl chloride was then prepared by heating the acid (36 grams) for one/

one hour on the water bath with 60 cc. of thionyl chloride, excess of which was removed by distillation in vacuo, eventually with addition of a little benzene. The acid chloride distilled completely at 126-130°/7 mm. yielding a colourless liquid with $[\alpha]_D^{20}$ - 84.7° in chloroform (C = 3.200, l = 2). Read and Grubb quote - 84.8°.

ATTEMPTED PREPARATION OF dl-DIPHENYL GLYCEROL 1-MENTHOXY ACETATE.

Preparations were carried out under various conditions as follows:-

(1) l-Menthoxy acetyl chloride (2.3 g., 1 mole) was added drop by drop to a solution of 2.4 grams (1 mole) of anhydrous diphenyl glycerol in 20 cc. of anhydrous pyridine. Noticeable reaction occurred at once, and after the mixture had been kept overnight the colour changed from yellow to red. On pouring the mixture into water, a white semi-solid mass separated, which could not be solidified. The ether extract of this product was washed successively with dilute hydrochloric acid, dilute sodium hydroxide solution/

solution, and water. The extract was dried, and the ether completely removed under diminished pressure, when a yellow syrup was obtained.

(2) Three molecular proportions of the acid chloride (3.5 grams) were added to one molecular proportion of the glycerol (1.2 grams) in 25 cc. of pyridine and the product worked up as before. A yellow syrup (4 grams) was again obtained.

Further attempts to obtain a crystalline ester were then made by carrying out the acetylation at different temperatures, both in the absence and in the presence of pyridine. Temperatures above 60° produced charring and dehydration but 50° appeared to be quite a safe temperature, only a slight darkening of the solution taking place.

Attempts to purify the crude syrupy ester were made (1) by dissolving it up in the minimum amount of benzene and partially reprecipitating with light petroleum ether or (2) by dissolving it in alcohol and throwing out a portion by addition of a little water.

This fractional precipitation was repeated until the amount of syrup was reduced by about 75%. The/

The remaining syrup (1.0 g.) was hydrolysed with $^N/_2$ alcoholic potassium hydroxide and resulting terpene products removed by steam distillation. The aqueous solution remaining in the flask was extracted with ether and the extract dried over sodium sulphate. The ether was then completely removed and the residue (0.30 g.) recrystallised first from ligroin and then from benzene. Rhombic plates (0.13 g.) separated identical with the diphenyl glycerol (hydrated form) obtained from the hydrogenations.

CONCLUSIONS.

The results of the present investigation may be summarised briefly as follows.

Diphenyl triketone has been hydrogenated at ordinary temperature using platinum oxide - platinum black catalyst and pressures of 2 - 5 atmospheres. The reduction was controlled by adjusting the amount of catalyst and in this manner the previously unknown dibenzoyl carbinol and diphenyl glycerol were obtained in excellent yield, while the intermediate dihydroxy derivative was isolated as a compound which readily underwent isomerisation. Complete reduction of the triketone at room temperature gave α, γ-dicyclohexyl glycerol in almost theoretical yield.

Diphenyl glycerol is a sweet tasting compound, which is appreciably soluble in water, and exists in readily interconvertible hydrated and anhydrous forms.

An unsuccessful attempt to resolve the diphenyl glycerol by means of l-menthoxy acetyl chloride possibly indicates that a meso form had been isolated, but this point has not been definitely established.

α, γ-Dicyclohexyl-glycerol resembles diphenyl glycerol in that it forms a crystalline triacetate, but differs in that it does not form a hydrate and is only/

only slightly soluble in hot water.

Each of the above mentioned hydrogenation products has a definite crystalline structure, and gives a characteristic colour reaction with sulphuric acid.

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