THE SELF CONDENSATION OF
ACETYLACETONE

THE SELF CONDENSATION OF ACETYLACETONE.
THE ACTION OF PHENYLISOCYANATE ON BENZIL.
(WITH SPECIAL REFERENCE TO THE BENZIL BENZILIC ACID RE-ARRANGEMENT).

BY

CHAS. ALAN AYRE B. Sc.

MANITOBA 1932.

A THESIS PRESENTED

TO THE

FACULTY OF THE GRADUATE SCHOOL OF MANITOBA UNIVERSITY

IN PARTIAL FULFILLMENT FOR THE

DEGREE OF MASTER OF SCIENCE

1933.

The writer wishes to express his indebtedness to Dr. H. P. Armes for the suggestion of the problems presented here; for his helpful advice and for his able assistance in translating a number of references in the German.

CONTENTS.

THE SELF CONDENSATION OF ACETYLACETONE.

THE ACTION OF PHENYLISOCYANATE ON BENZIL.

Contents - Cont'd.

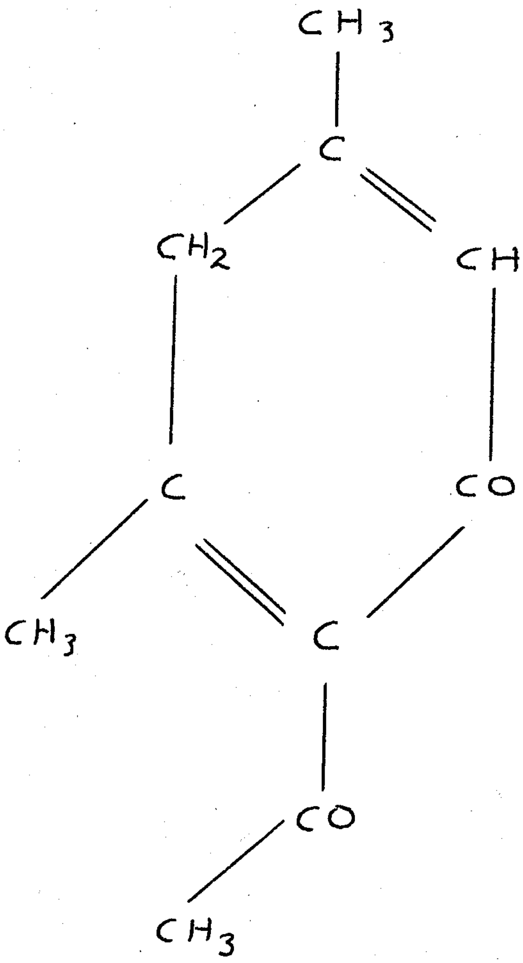
INTRODUCTION

THE SELF CONDENSATION OF ACETYLACETONE

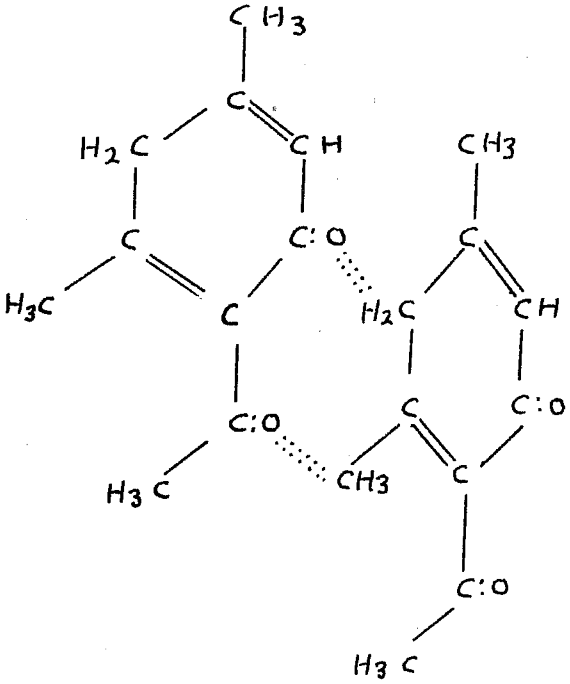
INTRODUCTION

Condensations undoubtedly play a most important part in the synthesis of complex naturally occuring compounds, from compounds of less complexity. The condensation presented here is one of dehydration, with or followed by reduction.

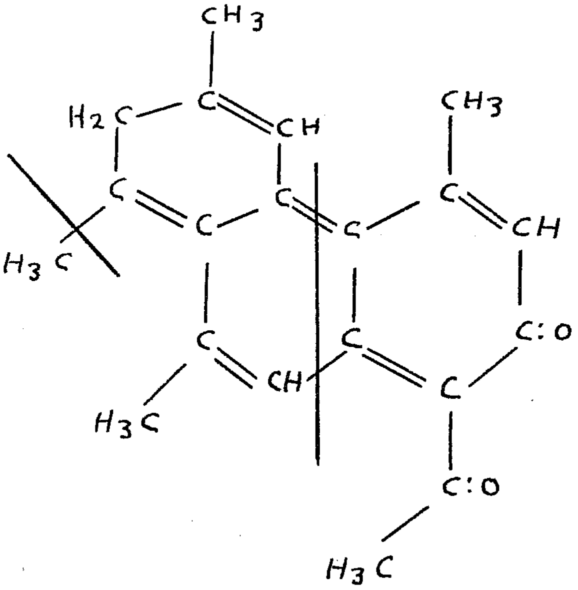
The object of the thesis was to determine whether the I.3 diketone acetylacetone could be caused to condense by the use of various dehydrating agents, and to produce terpene-like compounds. The problem is purely a theoretical one, and might feasibly take place in a series of condensations as shown below. Two molecules of the ketone may condense, linkage taking place between the terminal alkyl group- CH_3 of one molecule and the carbonyl :C:O group in the other: the formation of a ring then taking place, due to the elimination of one molecule of water from the active $:CH_2$ group of the one molecule and the second carbonyl group of the other, as shown in (I). This obviously does not lead to the formation of a typical terpene-like structure, but a compound of this type is quite capable of condensing as before with a second grouping as shown in (II). This complex compound might then decompose as shown in (III) with the formation of a compound having a terpene-like structure. It is apparent that the condensation could react further, in the same way, to produce still more complex structures.



I


CH3
H2C
CH
CH3
C
C:O
H3C
H2C
CH
C
C:O
C:O
H3C
CH3
C
C:O
H3C

I


CH3
H2C
C
CH
CH3
C
C
C
C
CH
H3C
C
C
C:O
C
CH
C
H3C
C:O
H3C

III

CONDENSATIONS OF A SIMILAR TYPE.

Condensations with loss of water are not at all uncommon, and a few examples will be presented. Such reactions may occur between hydrocarbon groupings and the hydroxyl groups of saturated alcohols; another case is that which occurs between aldehyde groupings and two CH groups; still another is the condensation between carbonyl groups and hydrogen atoms, to form hydroxyl groups as a first stage, with the final formation of a double bond by the loss of water.

Reagents which are commonly employed in such reactions are phosphorus pentachloride, fused zinc chloride, hydrogen chloride gas, aluminium chloride, and concentrated sulphuric acid.

As an example of the third type of condensation mentioned above, we may cite the important aldol condensation in which acetaldehyde by the action of hydrogen chloride gas condenses with itself as shown:-

$$CH_3\ CHO + HCH_2.CHO = CH_3.CH(OH).CH_2.CHO.$$

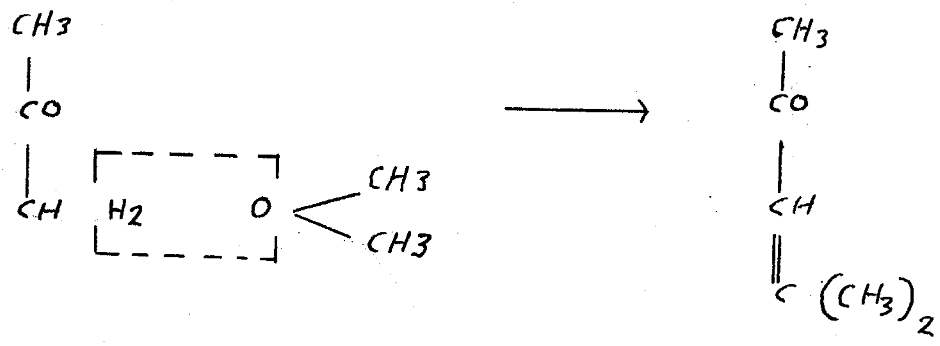
Aldol.

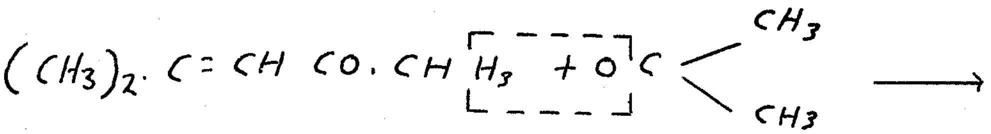
This is followed by the formation of crotonaldehyde by the elimination of one molecule of water:-

$$CH_3.CH(OH)CH_2.CHO = CH_3.CH = CH.CHO.$$

Aldol Crotonaldehyde.

Acetone undergoes a condensation[1], with the elimination of water, by the prolonged action of the dehydrating agent hydrogen chloride gas. Hydrogen chloride gas is passed into the ketone until it is saturated; the container is then lightly corked and allowed to stand for several days. The product is dark brown in colour, and has become somewhat viscous. Two unsaturated ketones have been obtained from this, namely, mesityl oxide $(CH_3)_2.C:CH.CO.CH_3$, and phorone $(CH_3)_2.C:CH.CO.CH:C(CH_3)_2$. These reactions may be represented structurally as follows.





$((CH_3)_2.C=CH\ CO.CH\boxed{H_3\ +O}C(CH_3)_2 \longrightarrow$

Mesityl Oxide

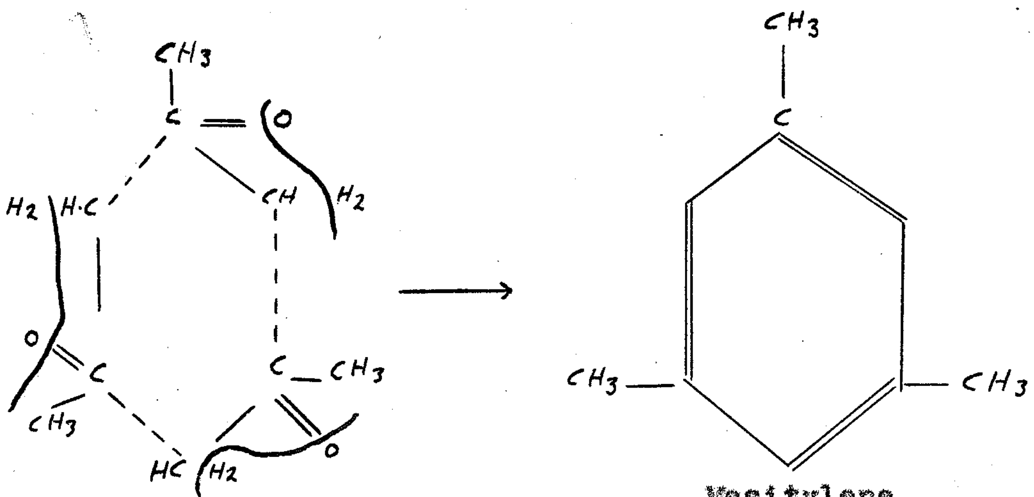
$(CH_3)_2.C:CH.CO.CH:C(CH_3)_2$

Phorone

Mesityl oxide is an oil, boiling at 130 degrees and possessing a characteristic peppermint like odour.

Phorone is a crystalline compound of melting point 28 degrees, and possesses an aromatic odour.

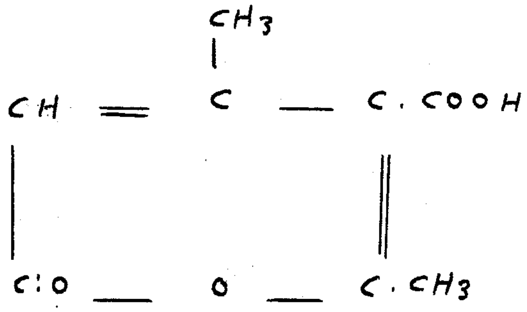
If, in place of anhydrous hydrogen chloride, eighty percent sulphuric acid be employed as the condensing agent a different product, mesitylene (I:3:5 trimethyl benzene), is obtained. The formation of this compound may be represented as occurring between three molecules of the ketone as shown:-



Mesitylene

Mesitylene is a colourless, mobile, pleasant-smelling liquid, boiling at 164.5 degrees, and is volatile in steam.

Ethylacetoacetate, which possesses a structure very similar to that of acetylacetone, undergoes a condensation when saturated, in the cold, with hydrogen chloride gas, and allowed to stand for several weeks[2]. The product darkens in colour, becoming a dark brown, and the viscosity increases. From this the additive compound iso-dihydroacetic acid and its ethyl ester have been obtained. A similar reaction occurs if sulphuric acid is used in place of the hydrogen chloride gas. Iso-dihydroacetic acid, is a pyrone derivative and has the structure:



Iso-dihydroacetic acid.

PREPARATION AND PROPERTIES OF THE I:3 DI-KETONES.

Acetylacetone, (pentane-2:4 dione), H_3 C.CO.CH_2.CO.CH_3, is obtained by the condensation of ethylacetate and acetone, according to a general reaction discovered by Claisen in 1889[3], This condensation involves the elimination of alcohol between the group .$COOC_2H_5$ of the ester and the CH_3 .CO- group of the ketone. This is effected by means of various reagents, two of which may be mentioned, metallic sodium and sodamide.

Acetylacetone was prepared by the method of Claisen, as given in Cohen's Practical Organic Chemistry.

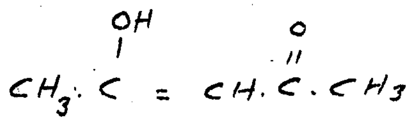
Twenty-five grams of sodium were pressed as wire into a two litre flask, containing a small amount of dry ether. The flask was fitted with a reflux condenser and cooled in a freezing mixture; 225 cc. of absolute ethyl acetate (previously cooled) were added. To this, 79 cc. of acetone, likewise cooled, were added in small quantities at a time. When all the acetone had been added the flask was allowed to remain for several hours in the freezing mixture, and then over night at the room temperature. The product was then shaken with water and slightly acidified with acetic acid.

To this solution 125 grams of copper acetate, freed from the basic salt, were added, whereupon the copper salt of acetyacetone was thrown down. The precipitate was allowed to stand for some time and then filtered off, suspended in ether, and decomposed with dilute sulphuric acid. The ether layer was separated and dehydrated over calcium chloride. The ether was then removed on the water bath, and the acetylacetone distilled, the portion boiling between 125 - 140 degrees being collected. Yield about 20 grams.

Acetylacetone is a colourless, pleasant-smelling liquid, of boiling point 136 degrees C.

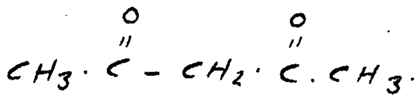
It should be noted that after the final distillation of the acetylacetone, a residue remains in the flask, which behaves in an identical manner to heat and chemical reagents as the condensation product to be described.

I:3 diketones, of which acetylacetone is an example, are acid in character, as shown by their formation of metallic derivatives which are insoluble in water, but soluble in organic solvents such as benzene and chloroform[4]. These metallic derivatives are usually represented as derivatives of the enol form (I), i.e. the metallic portion is assumed to be united to the oxygen atom. The free ketone is usually represented as the diketo compound, as shown in (II), although it is probable that it actually consits of an allelotropic mixture of the keto and enol forms.


$CH_3 \cdot \overset{OH}{\overset{|}{C}} = CH \cdot \overset{O}{\overset{\|}{C}} \cdot CH_3$

I

Enol


$CH_3 \cdot \overset{O}{\overset{\|}{C}} - CH_2 \cdot \overset{O}{\overset{\|}{C}} \cdot CH_3 \cdot$

II

Keto

L. Knorr and H. Fisher have isolated the pure form of the enol, by crystallising the equilibrium mixture from petroleum-ether, at a low temperature[5].

Claisen, who has done a considerable amount of work with the 1:3 diketones, reached the conclusion that the group-CO-$\overset{|}{\underset{|}{C}}$-CO- present in these substances plays the part of the =O atom in a carboxylic acid.

I.3 Diketones may undergo a variety of condensations; either the active -CH_2- group, or the carbonyl groups :C:O may take part, depending upon the type of agent employed to effect the condensation. Thus, orthoformic ester condenses in the presence of acetyl chloride with acetoacetic ester giving diethoxybutyric acid. If acetic anhydride be employed in place of acetyl chloride, an ester of the type $-CO-C(:CH.OC_2H_5)-CO-$ is obtained.

I.3 Diketones have also been employed in the preparation of pyrazole derivatives, by the condensation of the ketone with hydrazones.

EXPERIMENTAL WORK.

In the case of acetylacetone, preliminary test-tube experiments showed that a self-condensation took place, when various dehydrating agents were employed. About one gram of acetylacetone was added to each of four dry test-tubes. One was saturated with dry hydrogen chloride gas, a second was treated with anhydrous aluminium chloride, the third with fused zinc chloride, and the last with mercuric chloride. The tubes were stoppered and left for a period of forty-eight hours.

In the tube to which had been added the hydrogen chloride a somewhat viscous, dark brown product formed. A similar reaction took place in the tube containing the aluminium chloride. The fused zinc chloride had no apparent effect. The mercuric chloride was found to be extremely soluble in the ketone, but did not effect a condensation; the chloride was merely in solution, as later determined, and had not formed a compound.

A solution of the ketone in dry ether, when subjected to the treatment with anhydrous hydrogen chloride, showed a similar darkening of the solution upon the addition of the chloride and, as the process continued it was noted that the condensation product separated from the ether, due undoubtedly to the formation of a hydrochloride.

Since preliminary tests had indicated that a condensation had actually occurred it was decided to continue on a slightly larger scale, using anhydrous hydrogen chloride as the dehydrating agent, because of its convenience. Five grams of acetylacetone, contained in a sixty c.c. Erlenmyer flask were saturated with hydrogen chloride. A reaction occurs with the first addition of the gas, as indicated by a change in colour from the colourless acetylacetone to a light yellow tint, which gradually darkens to a deep reddish-brown. When saturated the flask was lightly stoppered and left to stand for a period of forty-eight hours. After this length of time, the product becomes deeper in colour and the viscosity increases to a very large degree.

To free this product from hydrogen chloride and to break down the hydrochloride which is undoubtedly formed, it was shaken with a dilute solution of potassium chloride, and then extracted with ether. It is worthy of note that the products of condensation, in ether, at this stage are fluorescent, being reddish by transmitted and green by reflected light.

The product, in ethereal solution, was dehydrated over potassium carbonate, and the ether subsequently removed. The residue, which was reddish brown in colour and extremely viscous, was placed in a vacuum dessicator over sulphuric acid and left till the next day.

DISTILLATION OF THE CONDENSATION PRODUCT.

In order to obtain a pure product from this it was dissolved in ether, transferred to a distilling flask and the ether removed on the water bath. When the ether had all been removed, the flask was heated with a free flame. Decomposition took place immediately, and a heavy, yellow coloured gas distilled over. The boiling point was not constant. This gas condensed to a thick gummy mass differing little from the original product. The distillate was again subjected to further distillations in an attempt to isolate a single ~~signel~~ pure product, but each time decomposition took place, and the various distillates showed no evidence of purity. After each distillation, a black carbonaceous residue remained in the flask. This was not examined at this time, as it was thought to be carbon.

DISTILLATION OF PRODUCT UNDER REDUCED PRESSURE.

Since there appeared to be no hope of isolating a pure product by this method, distillation in vacuo was next attempted. Decomposition again took place but to a somewhat less extent. Repeated distillation, in vacuo, yielded a small quantity of material which appeared to be fairly pure, and which possessed a pronounced phenolic odour. This material was placed in a Claisen flask for a final distillation, when suddenly, the whole mass crystallized. The supercooled liquid, for such it must have been, was probably caused to crystallize due to the scratching of the capillary tube on the bottom of the distilling flask. The crystals were dissolved in ether, from which they separated out as long needles, and in an impure form. Various solvents and combinations of solvents were employed in an attempt to purify the compound but without success, because all of them dissolved the tarry impurities to the same extent as the pure compound. Solvents employed included benzene, petroleum ether, acetone, ethyl acetate, chloroform, alcohol, toluol, xylol, etc.

These crystals were definitely phenolic in character. A small quantity dissolved in alcohol when treated with a cold solution of p-nitroaniline (decolorized by sodium nitrite) in dilute hydrochloric acid, and then with a few cubic centimetres of a solution of sodium hydroxide, gave a deep red colouration, indicating the presence of a phenolic compound. The melting point was determined, but due to the impurities was not sharp, lying between 60-65 degrees C., corresponding to I, 2 xylenol (4). Unfortunately before the exact nature of the compound could be determined by crystals were all used up, and although the process has been repeated many times since, the same compound has never again been obtained by this method.

DISTILLATION OF CONDENSATION PRODUCT WITH ZINC DUST.

In an attempt to obtain a compound of less complexity, some of the condensation product, in ether, was mixed with zinc dust, the ether removed and the mixture distilled. The distillate, however, showed little sign of yielding such a product, and the method was rejected.

It should be noted that the various distillates obtained polymerize, when allowed to stand for a time.

A CHEMICAL EXAMINATION OF THE CONDENSATION PRODUCT.

Distillation methods having proved unsuccessful, it was next decided to attempt to isolate a product from the condensation, by chemical means.

This product is a thick gummy liquid, brownish in colour and possessing a faint phenolic odour, on standing the viscosity increases and the colour darkens. It is insoluble in cold and hot water, and is neutral to litmus. It is not reduced by zinc dust and hydrochloric acid, or by sodium in alcohol. On oxidation with chromic acid in glacial acetic acid, a semi-solid, yellow coloured mass is obtained, which seems to be a mixture of various substances. All attempts to obtain a single pure product from this were unsuccessful.

When a small quantity of the condensation product was heated with strong potassium hydroxide solution and filtered, and filtrate was slightly coloured, and on acidifying this a small amount of material was thrown down. This was filtered off, dissolved in ether and the ether allowed to evaporate. The product is a resinous mass, with slight acidic properties.

The condensation product is apparently saturated since it does not decolourize potassium permanganate in dilute sulphuric acid, or bromine water.

Ketone and aldehyde groupings are apparently absent. The product dissolved in alcohol was warmed for some time with a mixture of semicarbazide hydrochloride and sodium acetate, and then poured into a large volume of water; the original substance was thrown out of solution. Similar attempts using hydroxylamine hydrochloride, and phenylhydrazine were unsuccessful.

Further, attempts to prove the presence of an alcohol grouping were unsuccessful.

From this it must be concluded that the product is a mixture of saturated hydrocarbons.

AN EXAMINATION OF THE RESIDUE FROM THE DISTILLATION OF THE CONDENSATION PRODUCT.

When the condensation product from acetylacetone is distilled under reduced pressure, decomposition takes place and a considerable amount of residue remains in the flask. This residue is black in colour and possesses a shiny lustre. Because of its appearance it seemed likely that it must be something other than amorphous carbon; such was indeed found to be the case.

When refluxed for several hours with alcohol, practically nothing had gone into solution. The solid was then filtered off, dried and treated with nitrobenzene. A considerable amount was found to go into solution; the insoluble portion was filtered off and the nitrobenzene solution subjected to steam distillation. When the nitrobenzene had all been removed, a small amount of black solid remained in the flask. This same solid was obtained from the nitrobenzene solution by the addition of petroleum ether, in which it, the solid, is insoluble. Chloroform was found to be an ideal solvent, and was employed ~~thee~~ henceforth for all extractions etc.

The insoluble portion remaining after extraction with either nitrobenzene or chloroform, does not appear to be amorphous carbon. It seems to be entirely insoluble and chemically inert. Thus, when small quantities were treated with various solvents, and examined under the microscope, no indication of solubility was found. Some of the solvents employed were, chloroform, pyridine, phenol, ethyl carbonate, nitrobenzene, acetone, ethyl acetate, benzene, petroleum ether, alcohol etc. It is not acted upon by hot concentrated nitric or sulphuric acids, and is not reducable. Hydrocarbons, known as the α, β and γ compounds, having similar properties, have been isolated from coal, and it is possible that this residue might be related.

The portion which is soluble in chloroform separates from that solvent in shiny black plates. Under the microscope, a dilute solution in chloroform appears to have an amber tint; in more concentrated solution it appears black.

The compound shows no sign of melting at a temperature as high as 360 degrees C., as determined in a potassium sulphate-sulphuric acid bath. When heated to a high temperature it swells up, and decomposes without melting. The residue is insoluble in chloroform, and is probably carbon.

Reduction methods were first employed in an endeavor to determine the nature of the black plates obtained from the chloroform solution. All attempts were unsuccessful. Thus, it was unaffected by reagents such as stannous chloride and glacial acetic acid; zinc dust and glacial acetic acid; a mixture of concentrated sulphuric acid, glacial acetic acid, and aluminium powder; or tin and hydrochloric acid. When dissolved in chloroform containing a small amount of alcohol, and treated with sodium metal, no reduction took place. Again, it was not affected by the prolonged action of a mixture of red phosphorus and hydriodic acid, at a temperature of 100 degrees C.

Reduction methods having failed, oxidation methods were next employed, but without success. It was not oxidized by chromic acid in hot glacial acetic acid, or by heating with perchloric acid. When refluxed for some hours, first with dilute and then concentrated nitric acid no change was noted. When heated with sodium peroxide it underwent combustion. It was completely broken down by a hot solution of mercuric sulphate in concentrated sulphuric acid.

Because of its extreme stability it must be concluded that the compound is a hydrocarbon, probably cyclic in nature.

A quantity of the substance was carefully purified for use in molecular weight determinations and for analysis. The method employed was as follows:

The material was first refluxed with alcohol to removed any soluble impurities, filtered off, dried, and dissolved in chloroform. It was then precipitated from this solution by means of petroleum ether, filtered, and washed with alcohol and acetone. It was then redissolved in chloroform and precipitated with alcohol, and the precipitate was washed on the filter paper with acetone until the filtrate was colourless. It was then dissolved in chloroform and set aside to evaporate.

In the determination of the molecular weight by the freezing point method, the only solvent that could be employed was nitro-benzene, which as the results show, was not suitable. The material does not separate out of the solvent on freezing, but seems to form a solid solution.

Molecular Weight Determination.

Weight of watch glass + Compound = 5.3160 gms.
.. .. = 5.2867 ..
Weight of compound = .0293 ..

Freezing point of nitrobenzene, on Beckman theremometer = 7.3: 7.28: 7.3.

Average = 7.3

Freezing point of solution = 7.4

This freezing point was obtained repeatedly, and at the time was rejected as due to faulty manipulation, but further data was obtained which showed this not to be the case. The purity of the nitrobenzene might be questioned. but this is hardly likely, for it had been repeatedly distilled, the first and last portions distilling over being rejected in each case; and again, the freezing point of the pure solvent was constant.

Another determination gave a slight depression of the freezing point, but further determinations do not support this, and it is only given here for the sake of completeness.

Freezing point of nitrobenzene = 4.14°; 4.13° 4.16° and 4.14°.

Average = 4.14°.

Freezing point of solution = 4.10°.

Depression of freezing point = .04°.

Weight of watch glass + compound = 5.9415 gms.

Weight of watch glass = 5.9107 "

Weight of compound = .0308 "

$$\text{Molecular weight} = \frac{100.\ (kw)}{dW}$$

k for nitrobenzene = 71

W = 36 gms.

$$\text{Molecular weight} = \frac{100.\ (\ 71 \times .03)}{36 \times .04} = \quad 147.3$$

Another determination gave the following:

Weight of watch glass + Cpd. = 5.3362 gms.

Weight of watch glass = 5.2880 ..

Weight of compound = .0482 ..

Freezing point of pure solvent = 4.15 (mean).

Freezing point of solution = 4.17: 4.16: 4.16.

What ever the cause, it is apparent that the method is unsatisfactory and was abandoned. A new attempt was made to determine the molecular weight by the ebulistic method. The only solvent known which would be satisfactory, namely chloroform, underwent pyrolytic decomposition on coming in contact with the platinum used for heating. The products of the decomposition are tetrachloroethylene, hexachlorethane and hexachlorobenzene[6].

Attempts were now made to find for the compound other solvents which could be used for molecular weight determinations. This was not accomplished. Two solvents were found, namely pyridine and phenol, but they are not suitable for the purpose.

ANALYTICAL DATA.

Weight of $CaCl_2$ tube after combustion = 48.4670 gms.

Weight of $CaCl_2$ tube before .. = 48.4235 ..

Increase = .0435 ..

Weight of KOH tube after combustion = 61.3688 gms.

.. .. before .. = 61.0931 ..

Increase = .2757 ..

Weight of combustion boat - compound = 3.1688 gms.

.. .. = 3.0884 ..

Weight of compound = .0804 ..

Percentage of carbon = $\frac{12 \times .2757 \times 100}{44 \times .0804}$ = 93.5%

Percentage of hydrogen = $\frac{2 \times .0435 \times 100}{18 \times .0804}$ = 6.01%

Second Determination.

Weight of $CaCl_2$ tube after combustion = 44.1301 gms.

Weight of tube before combustion = 44.1006 ..

Increase = .0295 ..

Weight of KOH tube after combustion = 61.0931 gms.

Weight of KOH tube before combustion = 61.0110 ..

Increase = .0821 ..

Weight of combustion boat + compound = 3.1084 gms.

Weight of combustion boat = 3.0840 ..

Weight of compound = .0244 ..

$$\text{Percentage of carbon} = \frac{12 \times .0821 \times 100}{44 \times .0244} = 91.8\%$$

In this determination the combustion tube cracked before the oxygen had all been swept from the apparatus. This difficulty was overcome, in the case of the carbon, by passing dry air through the bulb, for a short time. This was not done with the $CaCl_2$ tube, because it was believed that the determination had been ruined and the tube was discarded.

The material is extremely difficult to ignite, so that it was decided to mix a little fine copper oxide with it, in the combustion boat, in order to facilitate the combustion. As the following data shows, this was not a success. The low carbon content can only be ascribed to incomplete ignition.

Weight of $CaCl_2$ tube before ignition = 48.4670 gms.

Weight of tube before combustion = 48.4910 ..

Increase = .0240 ..

Weight of KOH tube after combustion = 61.4876 gms.

Weight of KOH tube before .. = <u>61.3688</u> ..

Increase = .1188 ..

Weight of boat + copper oxide + Cpd. = 4.0572 gms.

Weight of boat + copper oxide = <u>4.0130</u> ..

Weight of compound = .0442 ..

Percentage of carbon = $\frac{12 \times .1188 \times 100}{44 \times .0442}$ = 73.8%

Percentage of Hydrogen = $\frac{2 \times 100 \times .0240}{18 \times .0442}$ = 6.6%

A <u>third</u> analysis gave the following.

Weight of KOH tube after combustion = 63.0070 gms.

Weight of KOH tube before combustion =<u>62.8058</u> ..

Increase = .2012 ..

Weight of $CaCl_2$ tube after combustion = 48.5830 gms.

Weight of $CaCl_2$ before the combustion = <u>48.5332</u> ..

Increase = .0498 ..

Weight of boat + compound = 3.6738 gms.

Weight of boat = <u>3.6090</u> ..

Weight of compound = .0648 ..

Percentage of hydrogen $= \frac{2 \times .0498 \times 100}{18 \times .0648} = 8.5\%$

Percentage of carbon $= \frac{12 \times .2012 \times 100}{44 \times .0648} = 84.6\%$

A fourth analysis gave:-

Weight of KOH tube after combustion = 45.0970 gms.
Weight of KOH tube before combustion = 44.8962 ..
Increase = .2008 ..

Weight of $CaCl_2$ tube after combustion = 34.3724 gms.
Weight of $CaCl_2$ tube before combustion= 34.3332 ..
Increase = .0392 ..

Weight of Boat - compound = 4.0970 gms.
Weight of boat = 4.0320 ..
Weight of compound = .0650 ..

Percentage of hydrogen $= \frac{2 \times .0392 \times 100}{18 \times .0650} = 6.7\%$

Percentage of carbon $= \frac{12 \times .2008 \times 100}{44 \times .0650} = 84.2\%$

The low results for carbon in these last analyses cannot be ascribed to the presence of oxygen in the compound, since the first analysis and the extreme stability of the material preclude such a possibility.

Since molecular weight determinations were unsuccessful, it is only possible to give an empirical formula for the compound. It is a hydrocarbon, and must possess a cyclic structure as suggested above. The formula, based on the first analysis, is as follows:

$$93.5 \div 12 = 7.7$$

$$6.01 \div 1 = 6.0$$

which gives C_5H_4 as the empirical formula.

REDUCTION OF PRODUCT DURING CONDENSATION.

Experiments were now tried to determine whether a simpler product could be obtained by reducing the product while it was being formed. This was done by dissolving the acetylacetone in ether, adding a small quantity of zinc dust and then saturating the solution with hydrogen chloride gas. On standing over night it was found that the product had separated from the ether. The undissolved zinc and the zinc chloride formed were removed by the addition of a dilute solution of potassium carbonate, and by filtering. The filtrate was then extracted with ether, dehydrated over anhydrous sodium sulphate, transferred to a distilling flask and the ether removed on the water bath. After the removal of the ether, the residue was gently warmed with a free flame; decomposition took place and a product distilled over. The boiling point was not constant. The distillate is a liquid, light yellow in colour and possesses a peculiar penetrating odour. It polymerizes on standing, yielding a brown viscous liquid.

A residue which is soluble in acetone is left in the flask after the distillation; this, on evaporation of the acetone, remains as a black tar.

The distillate is apparently unsaturated, since it removes the colour from bromine in carbon tetrachloride.

A portion of the distillate on warming with a small quantity of phenyl isocyanate formed a solid mass. This was shaken with petroleum ether, filtered and washed with ether to remove excess of phenyl isocyanate. The residue is a white crystalline compound, with a melting point lying between 233-235 degrees C. The melting point and general properties correspomd to diphenyl urea. The filtrate, that is, the ether washings, on evaporation yielded a small quantity of a thick gummy liquid, too small in quantity to be identified. It must be concluded that the distillate does not form a compound with the isocyanate. The diphenyl urea was probably formed by the action of the phenyl isocyanate on traces of moisture present.

A further quantity of acetylacetone (5 grams) was treated in the same way as given above, and distilled. The distillate was examined for the presence of terpenes. Terpenes are known to yield characteristic nitroso chlorides when mixed with amyl nitrite and concentrated hydrochloride acid in the cold[7]. These compounds are precipitated by the addition of acetic acid. An attempt was made to prepare such a compound from the distillate, the presence of a terpene-like compound being suggested by the peculiar characteristic odour. The method employed was as follows: Equal quantities of the distillate and amyl nitrite were mixed, well cooled and concentrated hydrochloric acid added slowly (no exothermic action was noticed as is usally the case in the formation of the nitroso chlorides of the terpenes) and on the addition of acetic acid no precipitate was thrown down. This reaction was repeated, with the same result, so that it must be concluded that either no terpene-like compounds exist in the mixture, or if there are terpenes present they do not form characteristic nitroso chlorides.

A portion of the distillate, when subjected to the Schotten-Baumann reaction does not form a compound, and consequently cannot possess a hydroxyl group.

The amount of distillate obtained is very small, and since experiments failed to indicate the presence of a compound which could be isolated in a pure form, the method was abandoned.

REDUCTION OF THE CONDENSATION PRODUCT.

Experiments were now undertaken to see whether after condensation, the product could be reduced to a simpler state. For this purpose the acetylacetone was condensed in the usual way, neutralized with sodium hydroxide, and extracted with ether. The product, after the removal of the ether, was dissolved in glacial acetic acid, and an excess of zinc dust added. This mixture was warmed on the water bath for several hours, when it was noticed that the solution in the acid, originally dark brown, had become very much lighter in tint. The excess of acid was removed by shaking with dilute potassium carbonate solution, and the whole filtered to remove undissolved zinc dust. The filtrate was extracted with ether, dehydrated over anhydrous sodium sulphate, and the ether removed. The residue from this was warmed for two hours on the water bath with a dilute solution of sodium hydroxide. At the end of this time, an insoluble portion was filtered off, and the filtrate acidified with dilute sulphuric acid; a light-brown coloured precipitae was thrown down. This was extracted with ether, dehydrated over anhydrous sodium sulphate, filtered and the filtrate allowed to evaporate. A crystalline mass was obtained, possessing a characteristic phenolic odour, and seemingly identical with the phenolic derivative already described elsewhere. The product was impure, and in order to effect a purification it was benzoylated, in the hope of obtaining a compound which could be freed from the tarry impurities. This was not accomplished. Only a very small quantity of the crystalline compound had been obtained, so that the process was immediately repeated, but although the same method has been followed several times, the compound was not obtained again.

Since saturation of the acetylacetone with hydrogen chloride gas results in the formation of a product from which a pure compound could not be separated, attempts were made to determine whether a different product could be obtained by passing the hydrogen chloride gas through the ketone for only a short time, and allowing to stand over night. The desired effect did not take place. Unchanged acetylacetone remains, and a product identical with that derived from the method described above was obtained in small quantity.

The condensation product polymerizes on standing. It was decided to determine whether contact with air had an effect on the formation of the condensation product. The hydrogen chloride gas was passed into a small quantity of acetylacetone, contained in a small flask which was being evacuated by a water pump. After some time the current of hydrogen chloride was stopped, the flask evacuated and sealed. On standing for forty-eight hours, a product was obtained, which was identical with that obtained when air is not excluded. Consequently air is not a determining factor in the condensation.

EXPERIMENTS WITH BENZOYLACETONE.

Experiments were tried with benzoylacetone, in the hope that a solid derivative would be formed. However, this was not found to be the case. The benzoylacetone when dissolved in ether and treated with anhydrous hydrogen chloride, underwent only a very slight condensation, with the formation of a viscous liquid. The benzolacetone may be recovered. Similarly when benzoylacetone was dissolved in dry ether, and treated with anhydrous aluminium chloride no condensation took place. The ketone may be recovered.

SUMMARY.

Acetylacetone undergoes a condensation when treated with hydrogen chloride gas and allowed to stand for forty-eight hours or longer. From this product, after neutralization and distillation, a hydrocarbon, similar to the α, β, & γ, compounds obtained from coal, has been isolated.

Experiments have shown that the self-condensation of acetylacetone does not result in the formation of terpene like compounds.

Reduction of the condensation product does not produce recognizable terpene compounds.

BIBLIOGRAPHY.

1. Cohen, Organic Chemistry Vol. 1 Page 228
   Baeyer, Annalen, 1866, 140, 297

2. Cohen, Organic Chemistry Vol. 1 Page 320

3. Cohen, Organic Chemistry Vol. 1 Pages 273, 275-7
   Claisen, Ber. 1889, 72, 1009; 1905, 38, 709

4. Schmidt, Organic Chemistry Page 219

5. L. Knorr and H. Fischer, Ber., 1911, 144, 2771

6. Hurd, Pyrolysis of Organic Compounds, Page 132

7. Heusler, Chemistry of the Terpenes, Page 74

THE ACTION OF
PHENYLISOCYANATE ON BENZIL

INTRODUCTION

THE ACTION OF PHENYLISOCYANATE ON BENZIL.

INTRODUCTION.

In this thesis a study of the action of phenylisocyanate on benzil, in the presence of anhydrous aluminium chloride, has been made.

The purpose of the investigation was to determine whether in the benzil-benzilic acid rearrangement an intermediate compound could be isolated.

According to R. Robinson[1], the benzil-benzilic acid change takes place due to the establishing of an intermediate ring system, set up through the agency of partial valency, which breaks down with a wandering of a phenyl group to establish the constitution of benzilic acid.

Armes[2] suggested a number of ways in which such intermediate compounds might be formed, and the present paper presents the work accomplished in their preparation and separation.

A BRIEF DISCUSSION OF THE BENZIL-BENZILIC ACID REARRANGEMENT

A brief introduction to the work which has been done on the benzil-benzilic acid rearrangement will be presented.

The wandering of a phenyl group from one carbon atom in benzil to the second carbon atom through the agency of aqueous alkali with the formation of benzilic acid has been the subject of much speculation and experimentation.

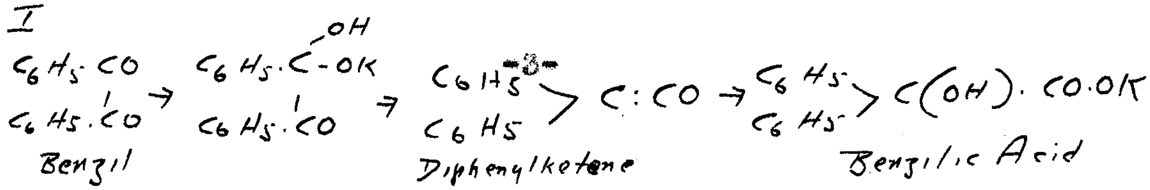
When benzil is heated with an aqueous solution of an alkali, a molecule of water is taken up and benzilic acid is formed:

$$C_6H_5COCOC_6H_5 + H_2O = (C_6H_5)_2\ C(OH)COOH$$

The hydroxyl ion is apparently of little importance; Lachman[3] has shown that when alkali is added to water the rate is increased twenty times, whereas the concentration of hydroxyl ions had increased about 10,000 times.

Schroeter[4], who was one of the first to advance an hypothesis, bases his explanation of the rearrangement upon the assumption that unsaturation of an atom is a source of instability, and consequently under certain conditions rearrangement would be expected. Thus, in the case of benzil Schroeter assumes that one molecule of say, KOH adds on to one of the carbonyl groups as shown in (I). This complex then breaks down with the formation of diphenylketene, which then reacts with the oxygen and potassium hydroxide to form the potassium salt of benzilic acid.

I



$$\begin{matrix} C_6H_5\cdot CO \\ | \\ C_6H_5\cdot CO \end{matrix} \rightarrow \begin{matrix} C_6H_5\cdot C\overset{OH}{-}OK \\ | \\ C_6H_5\cdot CO \end{matrix} \rightarrow \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!>C:CO \rightarrow \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!>C(OH)\cdot CO\cdot OK$$

In support of this Schroeter prepared azobenzil and was able to show that when heated in benzene it decomposed with the formation of diphenylketene.

Schroeter's view has been rendered untenable by the researches of Nicolet and Pele[5]. These investigators have shown that hydrogen peroxide, either in the free condition or in the presence of various alkalis has no action on diphenylketene.

A second theory, advanced by Nef[6], assumes that benzil adds on a molecule of water, and then dissociates into benzophenone and "dioxymethylene". This latter compound is further assumed to undergo change with the formation of formic acid, which then condenses with the benzophenone to give benzilic acid.

This view has been abandoned, since Lachman[7] has shown that benzilic acid decomposes into benzophenone, carbon monoxide, and water, and does not yield any formic acid.

Lachman has advanced the theory that a molecule of water adds to one of the carbonyl groups of benzil, and that one of these hydroxyl groups subsequently exchange places with a phenyl group:

$$C_6H_5C\ (OH)_2COC_6H_5 = (C_6H_5)_2\ C(OH)COOH.$$

That is, Lachman regards the process as an internal oxidation and reduction. In this respect it is somewhat similar to the addition of an organo-metallic compound to a ketone. This theory is supported to some extent by the discovery that a definite compound $C_{14}H_{10}O_2KOH$, can be isolated. The method employed is merely to grind the two constituents under pyridine or benzene. The compound is easily decomposed, with the regeneration of benzil and potassium hydroxide. However, when heated at a temperature of 80 degrees it is rapidly converted into potassium benzilate, and in consequence seems to be a true intermediate compound in the transformation.

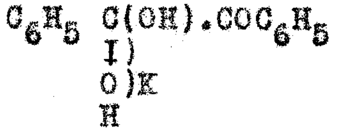
Further, Lachman has shown that benzil adds on one molecule of sodium ethoxide to form a compound:

$$C_6H_5C\ (ONa)(OC_2H_5)\ COC_6H_5,$$

which in the presence of water breaks down into its original components. In alcohol the products were found to be benzaldehyde and ethyl benzoate. When different amounts of water are now added to the alcoholic solution benzilic acid is produced. Lachman explains this as due to the presence or absence, as the case may be, of a mobile hydroxyl group in the intermediate compounds formed. Thus the grouping - OC_2H_5 is incapable of wandering under the conditions of the experiment.

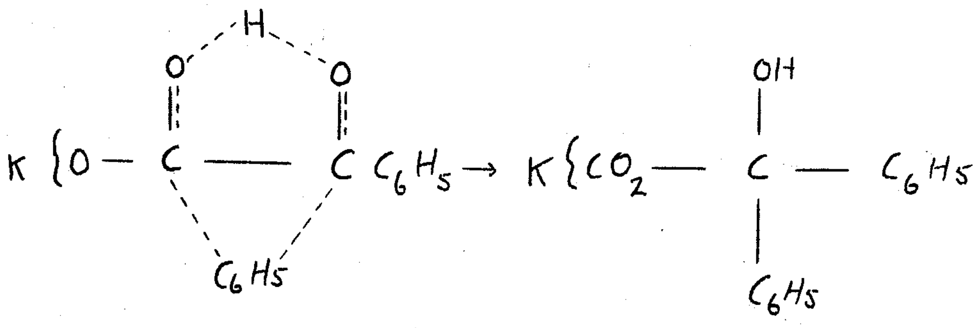
Lachman's theory is open to the criticism that it does not give any suggestion as to why the hydroxyl and phenyl groups should undergo wandering.

A theory which seems to embrace all the facts has been suggested by R. Robinson. He suggests that the reaction involves the rearrangement of the negative ion of the addative compound:



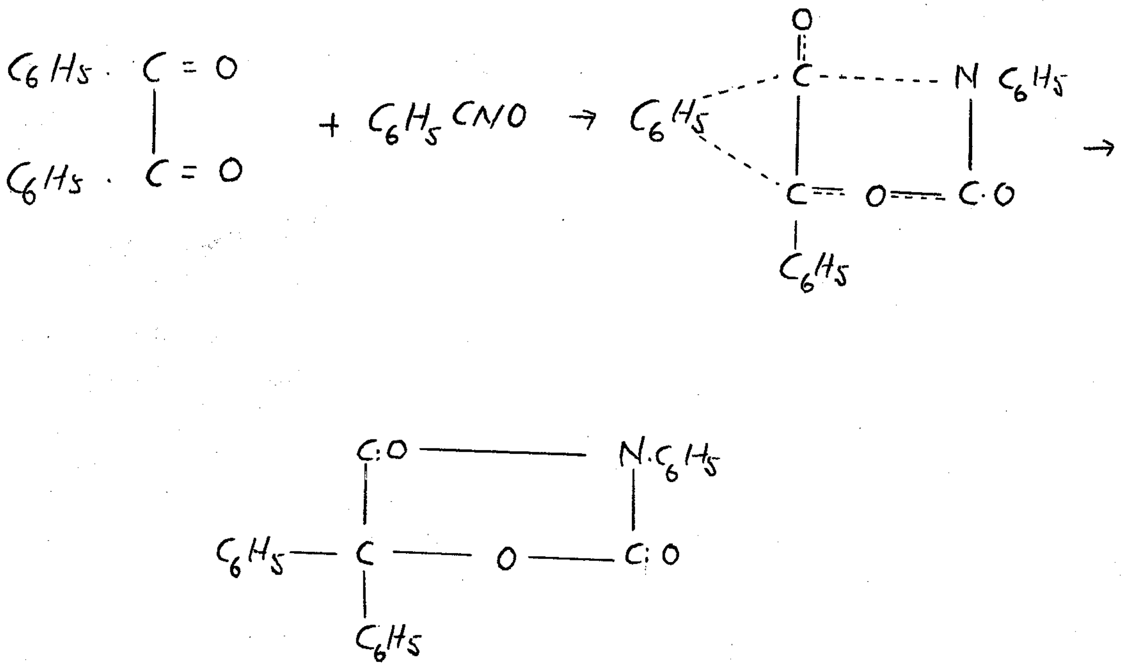
$$\begin{array}{ll} C_6H_5 & C(OH).COC_6H_5 \\ & |\,) \\ & O)K \\ & H \end{array}$$

To use his own words, "The charged = C(OH)-O- group strives to stabilise itself by becoming a true ion of a carboxylic acid. To do this, it loosens both a hydrogen atom and a phenyl group, which add on to the neighboring carbonyl. An intermediate stage can be represented on the partial valency theory by the expression."



THEORETICAL DISCUSSION.

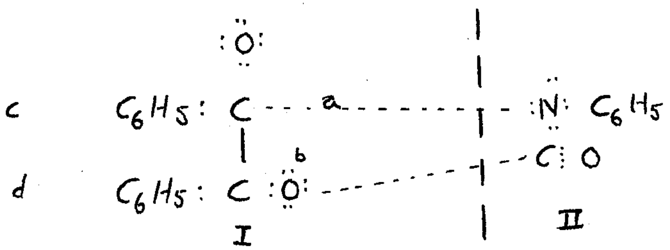
Working on a somewhat similar hypothesis to the one suggested by Robinson, Armes[8] has suggested that through the agency of aluminium chloride, phenylisocyanate might be caused to react with benzil to yield an intermediate compound which could be isolated. This would be represented:



On suitable decomposition, such a compound would be expected to yield either benzilic acid or a compound of that acid.

Further, Armes has suggested that the above may be represented in still another manner, i.e. by the more modern theory of co-ordination linkage.

The aluminium chloride, acting as an acceptor, activates the $\begin{matrix}-C=O\\ | \\ -C=O\end{matrix}$ grouping; this would in all probability co-ordinate the oxygen of the carbonyl group, and also the nitrogen of the phenylisocyanate, thus permitting the addition of one molecule of the latter compound. This would be represented diagramatically as follows:-



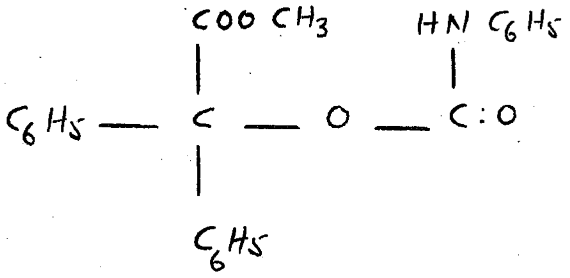
In I the benzil is shown in the "activated" state.

II shows the "activated" nitrogen.

At "A" and "B" we have co-ordinated nitrogen and oxygen atoms respectively.

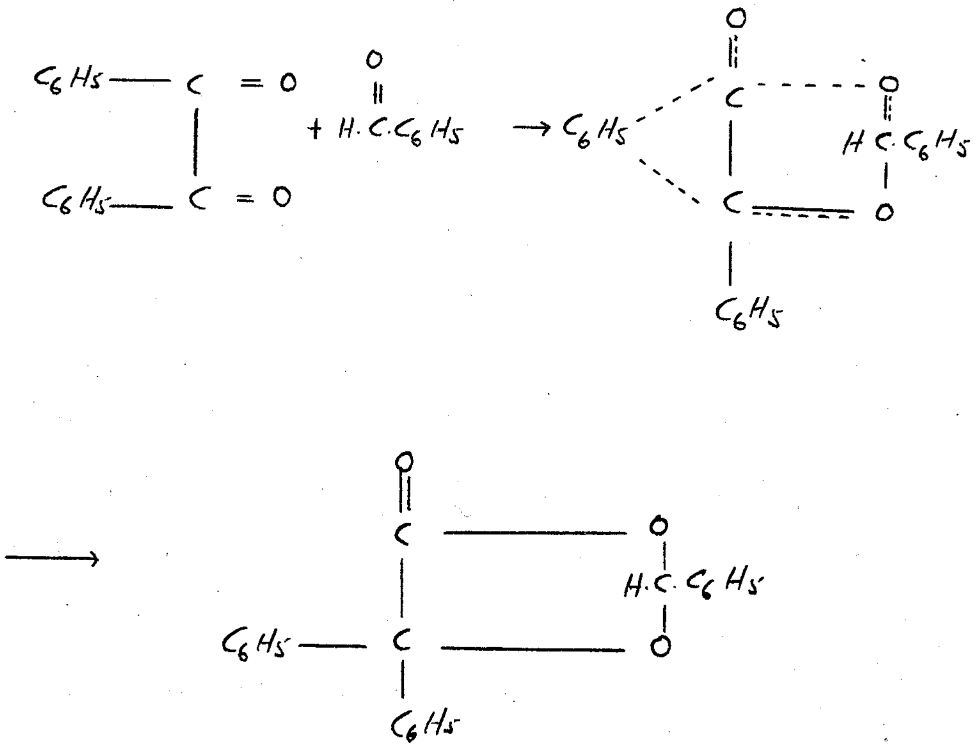
Rearrangement of such a compound would conceivably take place with the wandering of the phenyl group from "C" to "D", with the formation of the ring structure already discussed.

A compound such as the one described above, might also be synthesized in the following manner[8]. The methyl ester of benzilic acid when treated with phenylisocyanate yields a urethane of the following constitution:-



By loss of the elements of alcohol the ring structure given above would be formed.

A somewhat similar reaction is that which might possibly occur between benzaldehyde and benzil, and would be represented:



THE REACTION BETWEEN BENZIL AND BENZALDEHYDE, IN THE PRESENCE OF CONCENTRATED SULPHURIC ACID

A small quantity of benzil was dissolved in benzaldehyde and then treated with a few cubic centimetres of concentrated sulphuric acid. The acid was added in small amounts at a time, and the whole well shaken after each addition.

On the addition of the acid to the mixture, a deep reddish-brown colouration was produced, which darkens as the concentration of the acid increases.

When the mixture, plus the acid, was allowed to stand for some length of time, or when heated and then allowed to stand, a semi-solid mass was obtained. This was shaken with water containing a little sodium hydroxide, to neutralise the acid, transferred to a round bottomed flask and subjected to steam distillation, in order to remove the benzaldehyde. After the benzaldehyde had all been removed, a solid, which had separated in the distillation flask was filtered off and washed with water. This solid was a yellow-black in colour, insoluble in cold alcohol, readily soluble in acetone.

In order to purify the solid, it was dissolved in acetone, and to the solution so obtained, distilled water was added until a definite turbidity was produced. This was then allowed to stand over night and then filtered at the pump. The residue so obtained was nearly white in colour, and in the form of very small acicular crystals. The crystals were dissolved in hot alcohol, from which, on cooling, long, slender, yellow coloured crystals were deposited. On examination these crystals proved to be benzil. Evidently no extensive reaction had occurred between the benzil and the benzaldehyde.

The above experiment was repeated, with the exception that after the addition of the concentrated sulphuric acid, the mixture was heated for some hours on the water bath. A nearly solid mass was obtained, which was treated as described above. The main product again, on purification, proved to be benzil.

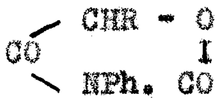
The blackish coloured impurities found in the above experiments, may be accounted for by the fact that, experiments have shown that concentrated sulphuric acid reacts with benzaldehyde alone to give colour reaction identical to the one described, and yielding a thick viscous product. This product is probably a polymer of benzaldehyde.

A small quantity of benzil was dissolved in benzaldehyde and to this solution a little anhydrous aluminium chloride was added. No reaction took place immediately, or on long standing.

From the above it is evident that, with the reagents employed, at least, no condensation takes place between benzil and benzaldehyde.

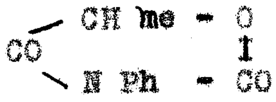
THE ACTION OF PHENYLISOCYANATE ON BENZIL.

A search of the literature disclosed the fact that compounds of the type described (i.e.oxazole derivatives) in the introduction, have been prepared. Thus, Eugéne Lambling[9], has shown that phenylcarbamide (phenylisocyanate) acts on compounds of the type COOR.CHR.OH to give rise to phenylurethanes of the formula COOR.CHR.O.CO.NHPh. The corresponding acids are obtained by successive treatments with alkali and acid. When boiled with water, these acids yield anhydrides of the constitution:

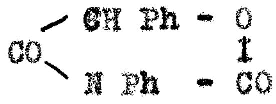


These compounds may be regarded as diketo-derivatives of tetra-hydro, oxazole.

The diketone,



crystallises in microscopic needles melting at 141 degrees. It is insoluble in a concentrated solution of sodium carbonate, and on warming, the sodium salt of the phenylurethane of lactic acid is formed. The diketone



of melting point 122 degrees yields when boiled with concentrated sodium carbonate solution, phenylurethane.

It is apparent that these derivatives are somewhat similar to the ring system which has been described elsewhere, and which might be formed by the action of phenylisocyanate on benzil.

In the preparation to be described the amount of aluminium chloride employed for the condensation was determined by experiment. It has been pointed out[10] that the quantity of aluminium chloride required to bring about condensations varies to a large extent with the constitution of the reacting substances. Traces are sufficient in some cases, in others a molecular portion of the aluminium chloride is required. In the reaction described, a trifle less than one molecular quantity of the aluminium chloride was found to give good yields.

Preparation and properties of the Condensation Product Produced by the Action of Phenylisocyanate on Benzil.

Benzil (210)	2 gms.	(1 Mol.)
Phenylisocyanate (119)	3.5 gms.	(1 Mol.)
Aluminium chloride (133)	1 gm.	(Slightly less than one molecular quantity)

The method given below, was employed throughout for obtaining the condensation product. The quantities of the reactants, of course, being chosen to suit the quantity of the product required at the time.

The benzil contained in a small Erlenmyer flask (the flask was employed because of the extremely painful lachrymatory action of the phenylisocyanate) was dissolved in the phenylisocyanate by warming on the water bath for a few minutes. The aluminium chloride was then added, in small amounts at a time. On the addition of the aluminium chloride an exothermic reaction took place immediately, and a deep scarlet-red colouration was produced. After the aluminium chloride had all been added, the whole was warmed on the water bath for some time, when it solidified. The colour faded somewhat. The heating on the bath was continued, and the product broken up with a stirring rod. It was then shaken with ether, filtered, and washed with ether until the odour of phenylisocyanate was not detectable. The ether removed most of the colour from the solid. The residue which was yellow in colour, was allowed to dry; ground to a powder and shaken with a warm solution of water containing a little dilute hydrochloric acid, in order to remove the aluminium chloride. The solid was allowed to stand over night in contact with the diluted acid, and then filtered, washed and dried. It was then dissolved in boiling alcohol, and the hot solution filtered immediately. The filtrate on cooling in running water deposits from solution a quantity of nearly colourless crystals. A further quantity may be obtained by evaporating the alcoholic solution.

The crystals so obtained were redissolved in hot alcohol, the solution cooled and the crystals which separated, were filtered off, dried and allowed to stand in a vacuum dessicator, over concentrated sulphuric acid, till the next day. The crystals so obtained are colourless, and in the form of long slender needles.

The melting point was found to lie between 178-180 degrees. The melting point was quite sharp, i.e. a slight melting is visible near the outside of the capillary tube at 178 degrees and at 180 degrees the whole quickly liquifies.

Larger crystals may be obtained by allowing the alcoholic solution remaining after the removal of the first crop of crystals, to evaporate slowly. They are colourless and in the form of long prisms, usually in bunches, radiating from a central nucleus M.P. 180° C.

On strong ignition the compound completely burns off, showing that it does not contain aluminium chloride, either in the form of a compound or adsorbed.

The compound is soluble in hot glacial acetic acid, from which it separates out on cooling. There is no change in composition, hence no chemical action has taken place.

On strong heating the compound decomposes, becoming brownish in colour. The odour of phenylisocyanate is detectable. The residue on purification, proved to be the original compound: evidently the decomposition was not extensive, or at least did not yield a product obtainable in quantity. Benzil, as might be expected, was not found.

The melting point and the fact that phenylisocyanate is evolved on heating, suggested that the product might be diphenyldiisocyanate. The easiest way to prove this seemed to be, to prepare some diphenyldiisocyanate and to compare the two compounds.

The diphenydiisocyanate was prepared by the method of Snape[11]. A small quantity of phenylisocyanate was refluxed with pyridine for about three hours. At the end of this time, the flask was cooled, and stoppered with a calcium chloride drying tube. This was then allowed to stand over night. The crystals of diphenyldiisocyanate, which had formed were filtered off, washed to remove excess of pyridine, and dissolved in alcohol. On evaporating off the alcohol, small, colourless quadratic plates, with a somewhat silvery, mica-like sheen, separated out. These crystals were dried in a vacuum dessicator and the melting point determined. M.P. = 175 degrees C.

Diphenyldiisocyanate is insoluble in pyridine the condensation product was found to be soluble in that solvent.

The condensation product is soluble in concentrated sulphuric acid, on slight warming, and at higher temperatures the solution becomes reddish-brown in colour. Diphenyldiisocyanate is soluble, but does not colour the solution on heating to a higher temperature.

A mixed melting point gave conclusive evidence that the two compounds were not identical.

ATTEMPTS TO BREAK DOWN THE COMPOUND.

Compounds possessing the oxazole ring system are frequently decomposed by heating with an aqueous solution of potassium carbonate, with the formation of urethanes.

For this reason, some of the derivative was refluxed for several hours with a concentrated solution of potassium carbonate. No change was noticed, and on filtering off the undissolved compound, recrystallising from hot alcohol, a melting point was obtained which showed that the compound had been unaffected by the treatment. The filtrate was shaken with ether (in order to remove any urethane that might have been formed) the ether layer separated, and allowed to stand for a time over anhydrous sodium sulphate, decanted and allowed to evaporate. No residue remained.

A small quantity of the material was refluxed for some hours with hydrochloric acid. At the end of this time the compound, which had shown no sign of reacting in any way, was filtered off, dried and recrystallised from hot alcohol. The melting point corresponded to the original.

The compound was found to be unaffected by prolonged heating with a dilute solution of hydrochloric acid and tin.

A small quantity of the material was dissolved in hot glacial acetic acid, a little chromic acid was added and the mixture heated for a few minutes. This was then allowed to stand over night, when it was poured into a large volume of water; a precipitate, with a slight yellow colour was thrown down. This was filtered off, dried and recrystallised from hot alcohol. The melting point was found to be so close to that of the original compound, that it was decided that the difference was due to impurities. This was found to be the case.

Refluxing the compound with aqueous potassium hydroxide has no effect, but prolonged refluxing with alcoholic potassium hydroxide yields a compound with a melting point of 185 degrees C and which gives a red colouration with concentrated sulphuric acid, similar to the colouration produced by the action of that acid on benzilic acid or its derivatives. There is unquestionably a wandering of the phenyl group from one carbon atom to another shown here, but since it is impossible to determine whether the wandering had occurred before the action of the alkali, or through the agency of the alkali the compound was not studied further.

ATTEMPTS TO SYNTHESISE THE COMPOUND FROM THE URETHANE OF BENZILIC ACID ESTER.

A small quantity of the methyl ester of benzilic acid was prepared. The method employed was as follows. The benzilic acid was dissolved in an excess of methyl alcohol, and into this solution hydrogen chloride gas was passed for a period of about 15-20 minutes. The solution so obtained was then refluxed for 8-9 hours, neutralised with a solution of potassium carbonate and extracted with ether. The ether-alcohol solution, so obtained, was allowed to evaporate; monoclinic crystals of the ester separated out, in a slightly impure form. Recrystallisation from ether yielded a pure compound, with a melting point of 74 degrees, C.

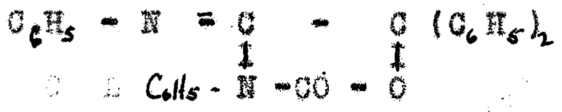
A part of the ester, thus prepared was then heated with phenylisocyanate until a solid was obtained. This was then washed with a small amount of ether and dried. The urethane was recrystallised from alcohol. The crystals are white in colour and in the form of tiny needles,: the melting point is 159 degrees C.

After preparing the urethane of the methyl ester of benzilic acid as described above, it was found that Lambling[12] had prepared the phenylurethane of ethyl benzilate, NH.Ph.CO.O.C.Ph.COO.Et. by a similar method. The phenylurethane thus prepared crystallises in slender white needles and melts at 151 degrees C. On heating with sodium hydroxide solution benzilanilide was formed, with a melting point of 174-175 degrees C.

Attempts were now made to repeat Lambling's work, but the ethyl ester could not be prepared in the pure form, i.e. crystals could not be obtained; the ester on removal of the ether, remained as a syrup. Ethyl benzilate has a low melting point, 34 degrees C., which is only a little above room temperatures. Because of this, it was decided to continue with the urethane prepared from the methyl ester. This compound is not mentioned in Beilstein.

For obvious reasons the closing of the ring was not attempted by the use of alkaline solution. Heating alone, for a period of about half an hour, just above its melting point failed to bring about any change. On strong heating the compound decomposes and the odour of phenylisocyanate is detectable. Heating with an alcoholic solution containing hydrochloric acid failed to produce any change. A method has not been found as yet, which will bring about the necessary closing of the ring.

A possibility suggested itself which might lead to the formation of a compound which could be closed by an internal Friedel and Craft reaction, i.e. the preparation of the phenylurethane of benzilic acid. However, it was found[13] that one molecule of benzilic acid reacts with three molecules of phenylisocyanate to give a compound which has the probable constitution:



Analysis of the Compound.

The results of four analyses for carbon and hydrogen are given.

First analysis.

Weight of combustion boat + compound = 3.3486 gms.
" " " " = 3.2694 "
" " " compound = .0792 "
Weight of KOH bulb after combustion = 52.4474 gms.
" " " " before " = 52.2172 "
Increase of weight = .2302 "
Weight of Calcium Chloride tube after combustion = 34.5924 gms.
" " " " " before " = 34.5540 "
Increase = .0384 "

Percentage of carbon $= \frac{3}{44} \times \frac{.2302}{.0792} \times 100 = 79.2\%$

Percentage of hydrogen $= \frac{2}{18} \times \frac{.0384}{.0792} \times 100 = 5.2\%$

Second analysis.

Weight of combustion boat + compound = 2.9596 gms.
" " " " = 2.8616 "
" " Compound = .0980 "

Weight of KOH bulb after combustion = 47.5360 gms.

.. .. before .. = 47.2470 ..

Increase = .2890 ..

Weight of calcium chloride tube after combustion = 34.6370 gms.

.. .. before .. = 34.5895 ..

Increase = .0456 ..

Percentage of carbon = $\frac{12}{44} \times \frac{.2890}{.0980} \times 100 = 80.4\%$

Percentage of hydrogen = $\frac{2}{18} \times \frac{.0456}{.0980} \times 100 = 5.3\%$

Third analysis.

Weight of combustion boat + compound = 2.9350 gms.

.. .. = 2.8616 ..

.. .. compound = .0734 ..

Weight of KOH bulb after combustion = 47.7546 gms.

.. .. before .. = 47.5360 ..

Increase = .2186 ..

Weight of calcium chloride tube after combustion = 34.6726 gms.

.. .. before .. = 34.6370 ..

Increase = .0356 ..

Percentage of carbon = $\frac{12}{44} \times \frac{.2186}{.0734} \times 100 = 81.2\%$

Percentage of hydrogen = $\frac{2}{18} \times \frac{.0356}{.0734} \times 100 = 5.3\%$

Fourth analysis.

Weight of combustion boat + compound = 3.4400 gms.

.. .. = 3.3530 ..

.. .. compound = .0870 ..

Weight of KOH tube after combustion = 44.5186 gms.

.. .. before .. = 44.2585 ..

Increase = .2601 ..

Weight of calcium chloride tube after combustion = 34.4236 gms.

.. .. before .. = 34.3780 ..

Increase = .0456 ..

Percentage of carbon $= \frac{12}{44} \times \frac{.2601}{.0870} \times 100 = 81.5\%$

Percentage of hydrogen $= \frac{2}{18} \times \frac{.0456}{.0870} \times 100 = 5.8\%$

Analysis of Nitrogen.

The nitrogen was analysed by the Kjeldahl method.

Weight of sample - .4224 gms.

25cc of (1.298N) acid required 31.8cc of atkali after distillation.

1cc of NaOH - .738cc acid.
31.8cc of NaOH - 31.8 x .738 = 23.464c acid.
1cc of acid - .0234 gms. NHy.

(25-23.46)cc $- \frac{14}{18} \times .02341 \times 1.54 - .0280$ gms. NH_4.

Percentage of Nitrogen $- \frac{.0280 \times 100}{.4224} - \underline{\underline{6.6\%}}$

Second Determination.

Weight of sample - .2868 gms.

30cc of acid required 39.2cc of alhali after distillation.

$$1.07cc \text{ acid} = \frac{14}{18} \times .02341 \times 1.07 = .0250 \text{ gms. } NH_4.$$

$$\text{Percentage of Nitrogen} - \frac{.0250 \times 100}{.2868} = 6.7\%$$

The carbon percentages show a variation, but the last two analyses check, and may be considered to be correct.

The hydrogen percentages are very constant.

The nitrogen percentages show a good agreement.

Assuming that one molecule of phenylisocyanate and one molecule of benzil condense as discussed elsewhere, the percentages of the various constituents are:-

Carbon = 76.6 Percent
Hydrogen= 4.5 "
Nitrogen= 4.2 "
Oxygen = 14.7 "

The results of the analyses may be summarized:

Carbon = 81.3 Percent
Hydrogen= 5.3 "
Nitrogen= 6.6 "
Oxygen = 6.5 "

It is apparent that there is no agreement, and that the condensation cannot have taken place, as suggested above.

The structural formula of the compound has not as yet been determined.

From the data given above the empirical formula has been calculated:

Carbon = 81.3 ÷ 12 = 6.7 ÷ .4 = 16
Hydrogen= 5.3 ÷ 1 = 5.3 ÷ .4 = 13
Nitrogen= 6.6 ÷ 14 = .47÷ .4 = 1
Oxygen = 6.5 ÷ 16 = .40÷ .4 = 1

which gives the formula $C_{16}H_{13}NO$.

A speculation as to the exact nature of the compound is left until further material can be obtained regarding its chemical reactions, etc.

SUMMARY.

A brief discussion of the Benzil-benzilic rearrangement has been given.

The action of concentrated sulphuric acid on benzil dissolved in benzaldehyde has been studied.

A compound, which has been analysed, has been isolated from the condensation taking place between phenylisocyanate and benzil, in the presence of aluminium chloride.

BIBLIOGRAPHY.

1. R. Robinson, Chem. Soc. Annual Reports, 1923. 118.
   J.B. Cohen, Organic Chemistry, Vol. 11.

2. Armes Personal Communication.

3. Lachman, J. Am. Chem. Soc., 44,330 (1922)
   Rice, Mechanism of Homogeneous Organic Reactions, 182-183.

4. Schroeter, Ber., 1909, 42, 2336.
   J.B. Cohen, Organic Chemistry, Vol. 11, 381.

5. Nicolet and Pele, J. Am. Chem. Soc. 1921, 43, 935.

6. Nef, See 3 (Rice).

7. Lachman, See 3.

8. Armes, Personal Communication.

9. Lambling, Compt. Rend. 1898, 177, 188-190.
   J.C.S. A I 84.

10. Rice, The Mechanisism of Organic Reactions.

11. Snape, J.C.S. 49, 254.

12. Lambling, See 9.

13. Beilstein, Vol. X11 Page 455.