

A STUDY OF THE
BENZIL-BENZILIC ACID REARRANGEMENT.

BY

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The writer desires to acknowledge his indebtedness to Dr. H. P. Armes for the suggestion of this problem; for the helpful advice given, and for the deep interest with which he has directed the investigation.

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INTRODUCTION.

This thesis is a report of the investigations made in connection with the type of rearrangement, known as the Benzil-Benzilic acid Rearrangement.

The modern Electrochemical(Electronic) theory¹ is being used more and more to explain organic reactions, and especially those reactions and rearrangements which have not as yet received any satisfactory explanation.

In this thesis, a tentative theory² is offered for the Benzil-Benzilic acid Rearrangement which is based on the above theory. A reason is given why the phenyl group should wander as it does, and also a reason why it should go to the carbon atom already possessing a phenyl group. A chelate ring structure is supposed to be set up during the rearrangement, but this stage cannot be isolated, as it represents an unstable system. However, Armes² suggested that by using Phenyl-isocyanate, which is a strongly polar compound, to react with activated Benzil, it might be possible to obtain a product showing that a chelate structure is formed. The Benzil could presumably be activated by using aluminium chloride.

Thus the work has resolved itself into an investigation of the action of Phenyl-isocyanate on Benzil and similar compounds, in the presence of aluminium chloride, and a study of the compounds thus obtained.

THEORETICAL DISCUSSION.

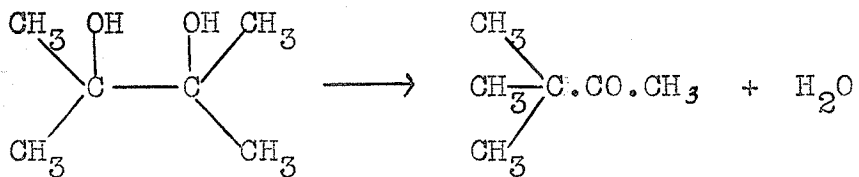
CARBON TO CARBON REARRANGEMENTS.

Among the different kinds of rearrangements³ in Organic Chemistry, there is the interesting type in which a grouping wanders from one carbon atom to another carbon atom. The wandering group may be an alkyl, an aryl or substituted aryl grouping, or it may even be a non-hydrocarbon group, such as a halogen. Such rearrangements have been the subject of much investigation, and numerous theories based on various viewpoints have been proposed as to the exact nature of the mechanism of the changes.

Several different types of carbon to carbon rearrangements will be mentioned to illustrate how large a field this phenomenon covers; an example will be cited in each type given.

I. THE PINACOL TYPE.

$\alpha\beta$ -Glycols with two tertiary, or with one tertiary and one secondary hydroxyl group undergo this change. Thus Pinacol, on being heated with sulphuric acid, gives an unsymmetrical ketone --- Pinacolone.⁴



II. THE BENZIL TYPE.

This rearrangement is experienced by aromatic

symmetrical 1,2-diketones. Benzilic acid is obtained when Benzil is warmed with an aqueous or alcoholic solution of a base.⁵



III. THE HYDROBENZOIN TYPE.

This type is related to type I, and is noticed with secondary glycols like Hydrobenzoin, which gives a good yield of Diphenylacetaldehyde when warmed with sulphuric acid.⁶

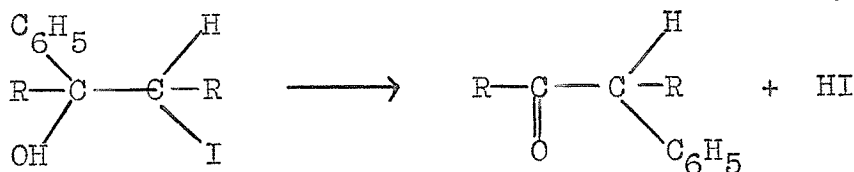


Similar to this change, but only giving a 10% yield, is the formation of Diphenylacetic acid from Benzoin when the latter is heated to 250°C with concentrated sulphuric acid.⁷



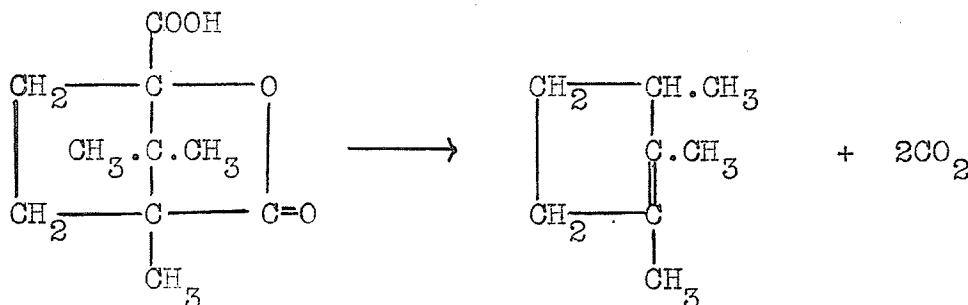
IV. THE IODOHYDROL TYPE.

This type was discovered by Tiffeneau.⁸ Iodo-hydrols when heated with mercuric oxide or with an alcoholic solution of silver nitrate, give ketones by the elimination of hydriodic acid.



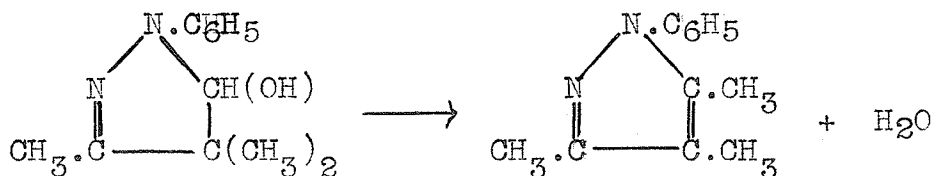
V. THE TERPENE TYPE.

Camphanic acid gives Laurelene by distillation.⁹



VI. THE PYRAZOLONE TYPE.

1-Phenyl, 3, 4, 4-trimethyl-5-oxypyrazolone is converted into 1-Phenyl, 3, 4, 5-trimethyl-pyrazol, by warming with mineral acids.¹⁰



VII. THE NON-HYDROCARBON TYPE.

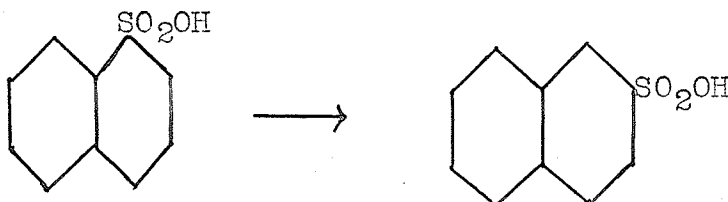
(a). Halogen moving.

α -Bromoacetoacetic ester gives the following change on standing in HBr.



(b). Sulphonic acid group moving.

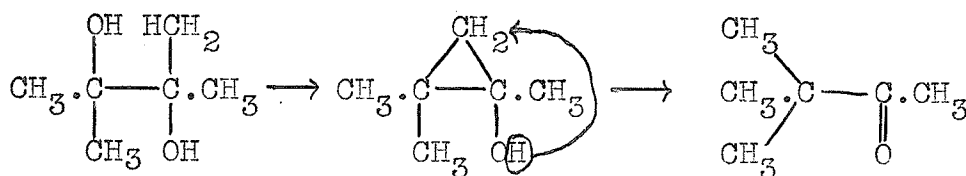
Naphthalene- α -sulphonic acid, when heated with acids, gives Naphthalene- β -sulphonic acid.



Of the above mentioned types, the first two listed have received, by far, the most attention. Since several theories have been advanced which attempt to explain both these types on a common basis, a brief discussion of the Pinacol change will be given.

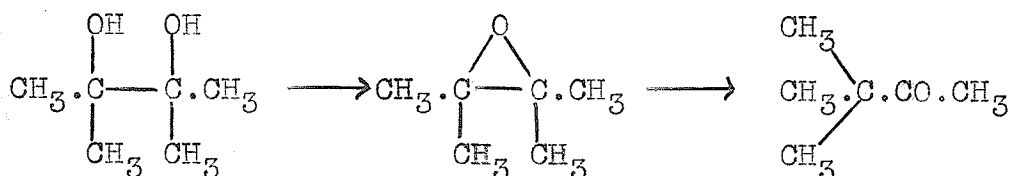
THE PINACOL CHANGE.

Erlenmeyer¹¹ suggested that water is split off and a cyclopropane compound is formed as an intermediate stage.



Other investigators¹² have considered the possibility of an intermediate compound having a cyclopropane ring, just as in the case of the rearrangements of monohydric alcohols.¹³ However, Montagne disproved this theory by his experiments on p-tetrachlorotetraphenylpinacol.¹⁴

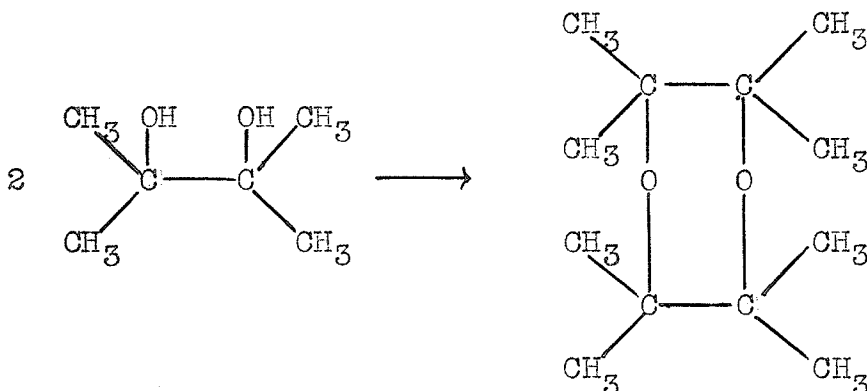
Breuer and Zincke⁶ postulated that an intermediate compound having an ethylene oxide structure is formed.



Working on the rates of transformation of pinacols and their corresponding ethylene oxides, Meerburg¹⁵ came to

the conclusion that the oxides were not an intermediate stage.

That a dialkylene oxide might represent an intermediate stage was suggested by Faworsky.¹⁶



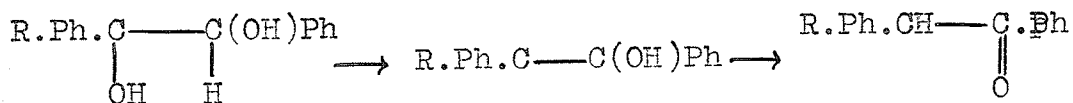
This theory was found to be unsatisfactory by Bayer.¹⁷

Tiffeneau and his collaborators¹⁸ based their views on Werner's theory¹⁹ of the varying value of single bonds; which, briefly stated is, that when an atom A of a compound AB is linked with other groups, its affinity may be decreased so that the total saturation capacity of B is not used; or in other words, the bond between A and B is not as strong as it would be if such a demand were not made on A by the other groups. On this basis, Tiffeneau divided the Pinacol change into the following types:-

i. The true Pinacol change.

The two hydroxyl groups are tertiary and one is less firmly held than the other; meaning that more demand is made on the affinity of one carbon atom than on the

this type. The tertiary hydroxyl group is removed with a hydrogen that is attached directly to the other carbon atom.

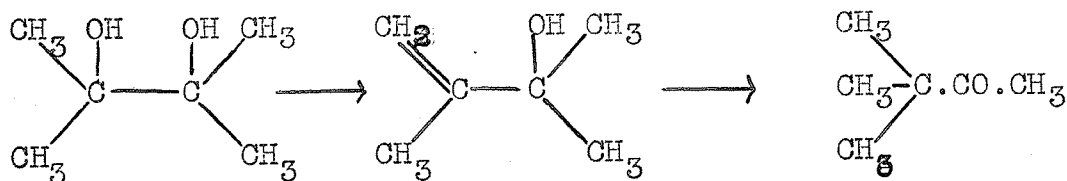


Tiffeneau agrees with Meerburg that an ethylene oxide compound does not represent an intermediate stage; he assumes the momentary existence of a univalent oxygen and a tervalent carbon atom.

Michael²² proposed his "affinity-energy-spatial" theory, and specifies three factors as determining the course of the rearrangement:-

- (a). The relative ease of the elimination of water in the various possible ways.
- (b). The energy requirements in the separation of the radicals capable of migrating.
- (c). The heats of formation of the possible rearrangement products.

The possible mechanisms, according to him, by which water may be removed from an $\alpha\beta$ -glycol are very similar to those assumed by Tiffeneau, except that he believes that aliphatic pinacols rearrange by water being eliminated through the union of one hydroxyl group with the hydrogen that is in an adjacent radical:-



It is found that tolyl and anisyl groups migrate easier than a phenyl group, and an ethyl group more readily than a methyl group.²³ However, as yet, no general rule has been formulated whereby the behaviour of secondary and tertiary glycols on dehydration can be predicted. Not only the groups present, but also the dehydrating agent used and the temperature have their effect on the course of the change. On the method of structural and valency interpretation, Tiffeneau's theory is generally accepted, but it is by no means satisfactory.

A theory based on partial valencies was proposed by Robinson.²⁴ He postulated that due to partial valencies a cyclic compound is formed as an intermediate step, which however cannot be isolated. A theory like this cannot be tested directly, but it has been applied with some success to several reactions.²⁵

There are several more theories of the Pinacol change, a few of which will be discussed in connection with the following rearrangement.

THE BENZIL-BENZILIC ACID REARRANGEMENT.

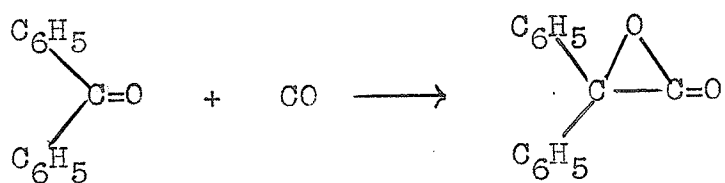
This is a rearrangement that takes place quickly, irreversibly, and gives nearly quantitative yield. It is one of the oldest known rearrangements,²⁶ but it has not yet received an entirely satisfactory explanation.

It is brought about, usually, by refluxing Benzil with alcoholic potash as shown by J.Liebig,²⁶ Zenin,²⁷ Jena²⁸ and H.v.Liebig.²⁹ Concentrated aqueous potash can be used as first described by Bösler³⁰ and later by Staudinger.³¹ The same type of rearrangement has been noted in other cases, such as Anisil to Anisilic acid,³⁰ Futil to Futilic acid³² and Phenanthraquinone to Oxy-fluorene-carboxylic acid.

In trying to explain this change, Nef³³ supposed that water adds on to Benzil forming a monohydrate, which presumably breaks down to Benzophenone and "dioxymethylene"; this latter hypothetical substance is supposed to give Formic acid by decomposition and this would unite with the Benzophenone to give Benzilic acid.

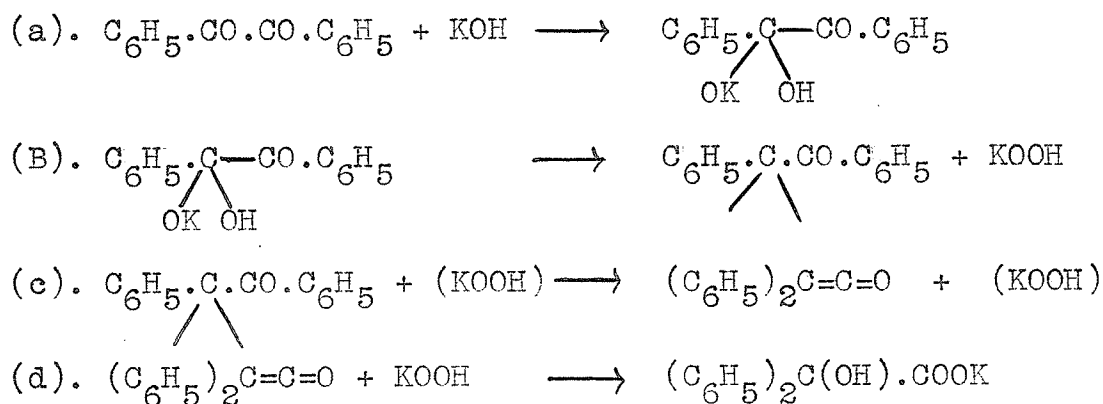
Testing this theory experimentally, Klinger and Standke³⁴ definitely proved that the change does not follow this path.

Nef³⁵ also suggested that Benzil dissociates into Benzophenone and carbon monoxide and that these re-unite to form a lactone, which on hydrolysis would give Benzilic acid:-

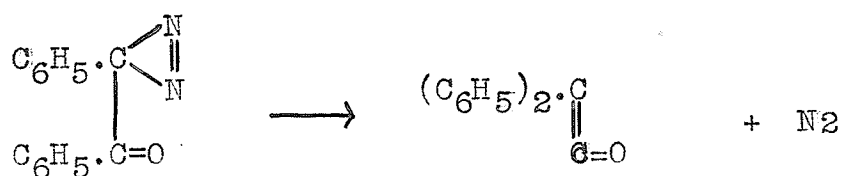


However, Acree³⁶ proved that carbon monoxide and Benzophenone when heated with alkali do not give any lactone or Benzilic acid. Also Lachman³⁷ showed that the series of changes are Benzil----→ Benzilic acid----→ Benzophenone and not Benzil----→ Benzophenone----→ Benzilic acid as Nef suggested.

Schroeter³⁸ assumed that the change takes place by the following stages:-

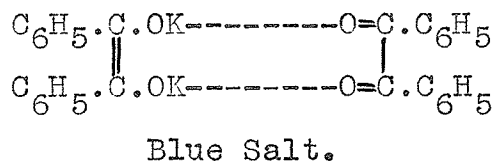
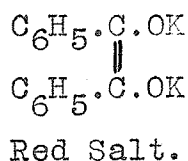


The assumption of the formation of Diphenylketene was justified by his experiments on Azibenzil, which readily loses nitrogen on heating, giving Diphenylketene.

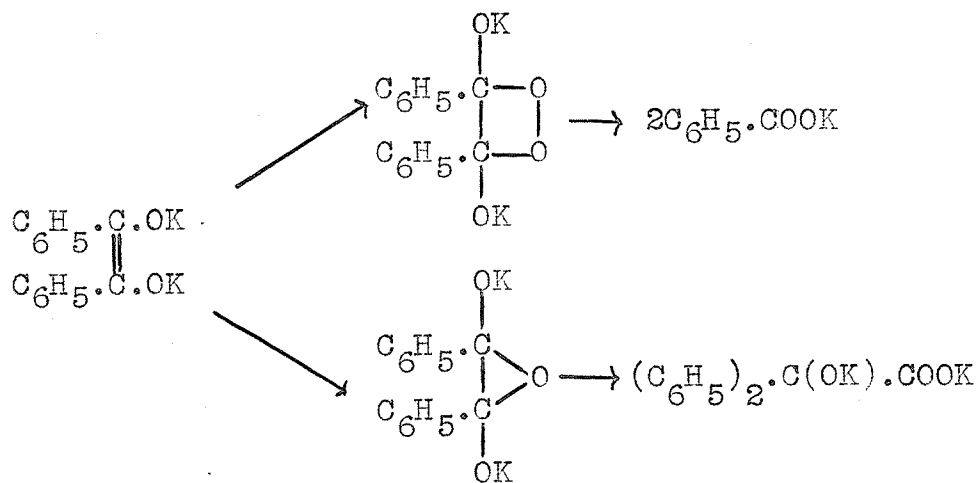


Nicolet and Pelc³⁹ showed that neither hydrogen peroxide nor its salts will combine with Diphenylketene to give Benzilic acid, proving that Schroeter's theory, in its above form, is untenable.

When one equivalent of potassium is added to a benzene solution of Benzil, a blue-violet colour appears.⁴⁰ When two equivalents of potassium are used a red compound is formed. This is a reversible process, the red changing to blue upon the addition of Benzil and the blue compound changing to the red one by the addition of potassium. These salts are prepared in an atmosphere of nitrogen to prevent oxidation. According to Staudinger and Binkert,⁴¹ the red salt is the dipotassium salt of stilbene glycol, and the blue one is a quinhydrol composed of one molecule of the red derivative and one of Benzil:-

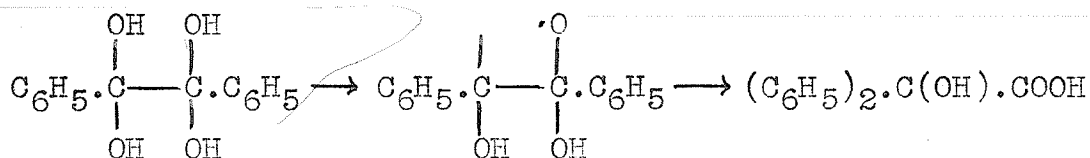


On bubbling air or oxygen through a warm solution of the red salt, the colour changes to violet which finally disappears with the precipitation of Benzilic and Benzoic acids. Staudinger represents this reaction:-



He suggested that the conversion of Benzil to Benzilic acid by aqueous alkali may be accomplished through a similar mechanism. It is noticed that Benzoic acid is generally present in varying amounts along with Benzilic acid, but the above theory is very hypothetical and not given to experimental investigation.

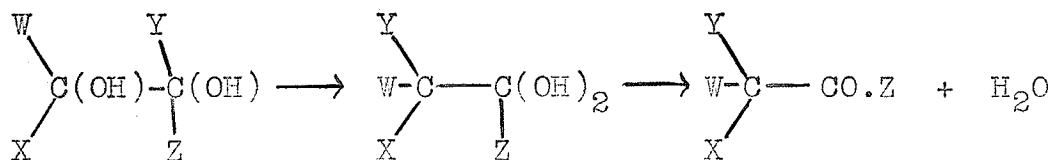
Tiffeneau⁴² postulated that water is added to each carbonyl group, and then applies the theory he developed for the Pinacol change.



The above theories have been found to be theoretically unsatisfactory by Michael,⁴³ and he offered his "affinity-energy-spatial" theory, regarding "the great positive energy of the alkali" as the propelling force of the change. Against this, however, Lachman³⁷ pointed out that Klinger⁴⁴ obtained Benzilic acid from Benzil by exposing it in moist ether to sunlight. Jena²⁸ succeeded in getting .25 grams of Benzilic acid from one gram of Benzil without the use of alkali. Lachman,³⁷ himself, was able to obtain Benzilic acid from Benzil by boiling the latter with water. From this the question arose as to whether the important role of the rearrangement was played by the hydroxyl ion, but Lachman showed that an increase of 20,000 in the concentration of this ion only increased the rate of trans-

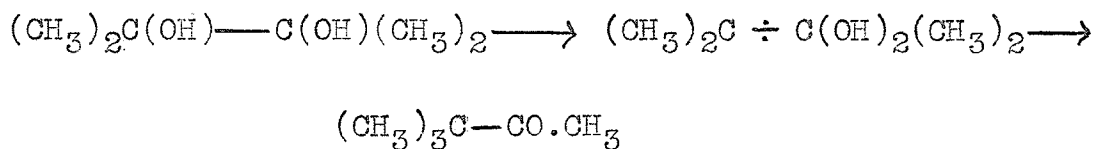
formation twenty times, proving that the hydroxyl ion, of itself, is not important.

By making one assumption, Lachman³⁷ arrived at a simple explanation of, not only the Benzil rearrangement, but also the Pinacol change and related transformations. The assumption is "that hydroxyl groups attached to adjacent carbon atoms tend to unite with one of these atoms and, in so doing, the mobile hydroxyl group exchanges place with some atom or radical". Thus, in general:-

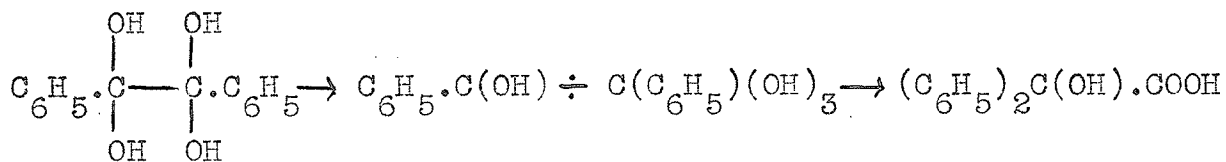


Where W, X, Y, and Z may be hydrogen, a hydroxyl or radical grouping.

Applied to the Pinacol change:-



Similarly in the Benzil rearrangement, by first assuming that Benzil is hydrated:-

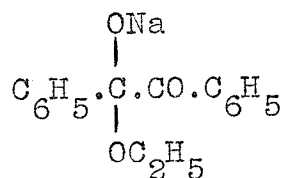


÷ represents that a hydroxyl group has moved.

Stability is reached by a hydrogen or a radical going the

other way(see below for the name applied to this shifting).

According to Lachman's later views,⁴⁵ only one carbonyl group is hydrated. Referring to the migration of the hydroxyl group, he says,³⁷ "The assumption of a mobile hydroxyl group is not new. Lieben⁴⁶ was among the first to suggest it for the Pinacol change....Meerwein,⁴⁷ whose recent work has brought out evidence strongly corroborative with the views here set forth....." He^(Lachman) pointed that the two rearrangements for which he developed the above theory, are also cases of intramolecular oxidation and reduction, and he suggested the name - Metakliny-(from the Gr., meaning "shift of cargo"). for these changes. In support of his theory the following facts are presented. Benzil reacts with sodium ethylate to give an addition compound. This was first described by Scheuing⁴⁸ and soon after by Lachman,⁴⁵ who at the time did not know of the former's work.



In absolute alcohol, Lachman found this compound to decompose into ethyl Benzoate and benzaldehyde, both of which may subsequently appear as benzoic acid. But in the presence of water(20% or more) the rearrangement to Benzilic acid is nearly quantitative. He attributed this

influence of the solvent to the mobility of the hydroxyl group which is produced by the hydrolysis of the NaO- group, thus making the rearrangement possible, whereas the rearrangement will not take place under conditions that preclude the existence of any hydroxyl group.

The above theory has simplicity in its favour, but granted that the hydroxyl group is mobile, Lachman gave no reasons or evidence for his assumption on which his theory is based.

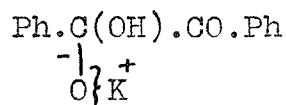
That Acree⁴⁹ had established in 1905 that only one molecule of reagent was required for the rearrangement, escaped the notice of other investigators, until Scheuing⁴⁸ re-established the fact by presenting his evidence that only one molecule of water, or of metallic hydroxide, or of an alcoholate adds to Benzil when the latter is treated in aqueous or alcoholic solution. Since then, several investigators have proved this fact --- Lachman,⁴⁵ Schönberg and Keller,⁵⁰ and Evans and Dehn.⁵¹

Apparently, the true intermediate product of the rearrangement is $C_{14}H_{10}O_2 \cdot KOH$, which has been isolated by grinding potash and Benzil under pyridine. This compound is decomposed, by treatment with water, into its components--- potash and Benzil. It is slowly converted, at ordinary temperatures, into potassium benzilate; the change can be

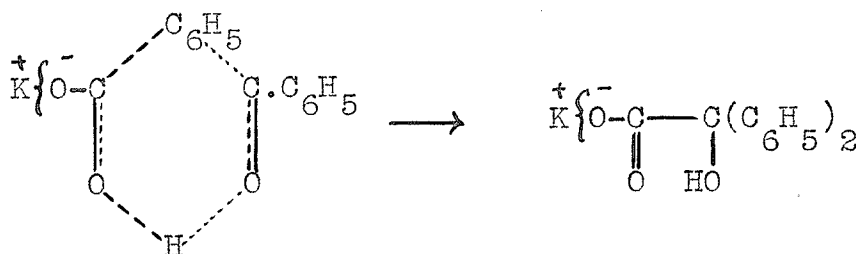
accelerated by raising the temperature.

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Taking this as the intermediate product Robinson proposed a theory based on partial valencies, which is briefly stated here. The rearrangement takes place in the negative ion of the additive compound

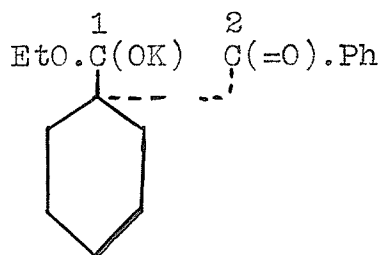


Thus the charged C(OH)-O- group tends to reach the stable form of a true ion of the carboxylic acid. To do this it loosens both a hydrogen and a phenyl group, these adding on to the neighbouring carbonyl group. The intermediate stage can be represented as:-



Another theory based on partial valencies was suggested by Schönberg and Keller.⁵⁰ "They believe that the migration in the rearrangement is due to the fact that these intermediate products $\text{Ph.C(OEt).(OK)-CO.Ph}$ and $\text{Ph.C(OH).(OK)-CO.Ph}$ contain a valence supersaturated carbon atom(1), and a valence undersaturated carbon atom(2). (The radicals Ph, OK, OEt, OH and CO.Ph use much valence, while the union of the carbonyl O with the carbon uses less valence than two normal unions). The carbon atom(2) and the carbon atom through which the phenyl residue is attached to

carbon atom(1) must therefore have strong partial valences which mutually satisfy each other."⁵³



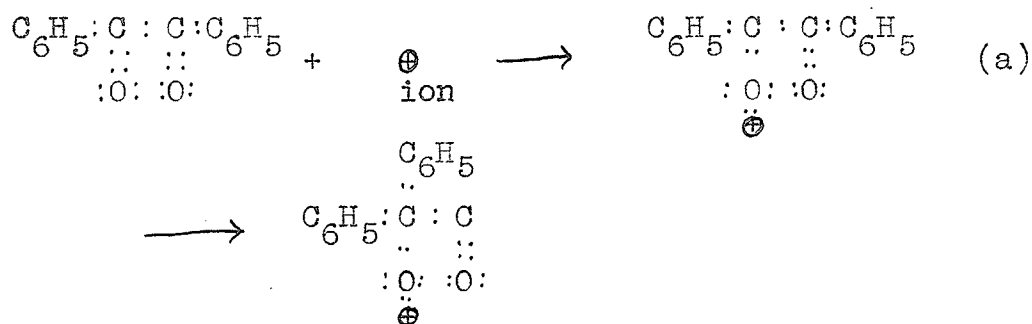
Within the past decade or so, there has been numerous attempts to explain organic rearrangements with the help of the Electronic Valency Theory. Although the various theories that have been developed on this point of view as applied to the Benzil-Benzilic acid rearrangement and the Pinacol change are based on the same fundamentals, there is still confusion as to the exact mechanism of the changes, no doubt due to the fact that most of the theories cannot be tested in any way experimentally.

Shoppe⁵⁴ presented a theory which is reported to be very general in its application to a large number of rearrangements. He has named it the "pinacolic electron displacement theory", which, it is stated, also accounts for the function of the reagents. The transformations are supposed to proceed according to the scheme:-



Since it was not possible to secure his original paper, the theory cannot be discussed any further here.

The following scheme was proposed by Whitmore⁵⁵:-



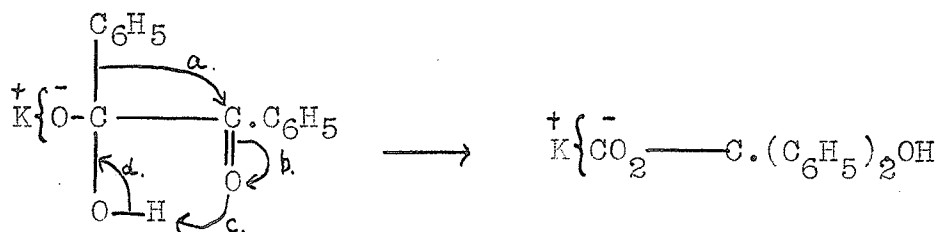
An oxygen atom in a carbonyl group is anionoid (electron-donating). After the stage(a), it is supposed that the carbon with the open sextet then attracts the electron pair and phenyl group from the adjacent carbon atom; and the addition of hydroxyl ion to the rearranged fragment converts it to Benzilic acid.

This scheme gives a reason why the carbon should accept a second phenyl group, but does not offer a reason why the latter should leave its original carbon atom.

Lapworth⁵⁶ proposed that groups and ions should be classified as anionoid or kationoid according to their behaviour; with this suggestion Robinson¹ pointed out that the carbon in a carbonyl group is definitely kationoid, meaning that it has a tendency to take on electrons.

Robinson's theory of the Benzil-Benzilic acid change, based on the Electronic Valency Theory is very similar to his theory that was based on the Partial Valence Theory, nearly a decade previous. As stated then, the anion

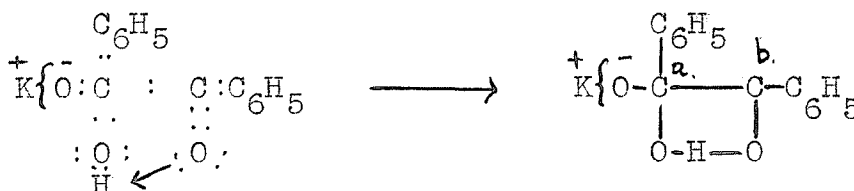
cannot retain the charge caused by the addition of one molecule of alkali hydroxide and, to use his own words, "it is suggested that the rearrangement occurs in order that the negative charge may be accommodated in the anion of a true acid. Presumably therefore the phenyl group migrates with its bonding electrons to the kationoid carbon of the C=O group(a); an intramolecular Grignard reaction. The processes (b), (c) and (d) will then be consequent electromeric changes necessary in order to preserve the octets! He represents the change:-



AN ALTERNATIVE THEORY AND A DISCUSSION
OF ITS RELATION TO THE PROBLEM.

A theory, which is very similar to Robinson's theory outlined above, is tentatively offered, which gives a reason why a phenyl group should leave one carbon atom, and why it should go to another carbon atom.

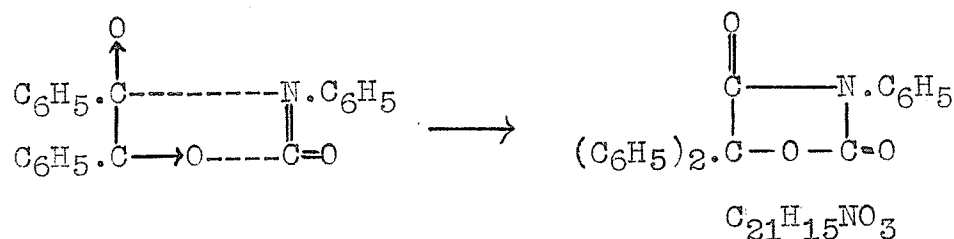
The formation of a chelate structure, which is not an uncommon occurrence, is postulated.



In words---the hydrogen of the hydroxyl group is kationoid(electron-accepting) in nature, while the unchanged carbonyl group has an oxygen, which is anionoid(electron-donating). Thus the co-ordination will take place as indicated, giving a chelate structure. This is, however, unstable since at (a) there are three groups which are anionoid, which is obviously too much for the carbon atom to hold; while at (b) there is a carbon atom short of electrons. Hence it will be readily seen why the phenyl group moves as it does. Of course the ring breaks down and each atom will then possess a complete octet of electrons; and the result is an anion of a true acid---Benzilic acid.

In an attempt to isolate a compound that would show the chelate ring structure, it was suggested² that the action of Phenyl-isocyanate on Benzil, in the presence of aluminium chloride be studied.

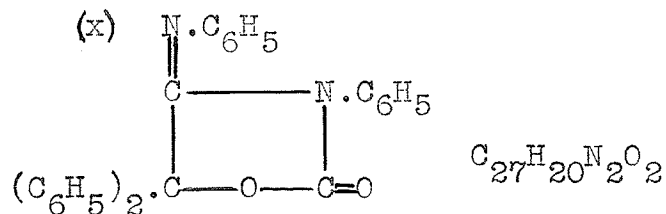
In this case there are no ions, but aluminium chloride is used as an activator, since, as Sidgwick⁵⁷ pointed out, it can readily increase its covalency from three to four and often to six. In this manner the carbonyl groups of the Benzil will be activated. The Phenyl-isocyanate is a strongly polar body; it has an anionoid (electron-donating) nitrogen atom and a kationoid (electron-accepting) carbon atom. The carbon in an activated carbonyl group is kationoid and the oxygen is anionoid. Combination will therefore take place as shown:-



The chelate structure is thus formed and, by the same reasoning as mentioned above, a phenyl group will wander giving the compound indicated.

The action of Phenyl-isocyanate on Benzil in the presence of aluminium chloride, did not, however, give a compound of the above composition, but of a composition

agreeing perfectly with:-



This means that an anil group(x) must have been introduced after the rearrangement; it is known that Phenyl-isocyanate can replace a keto group with an anil group.

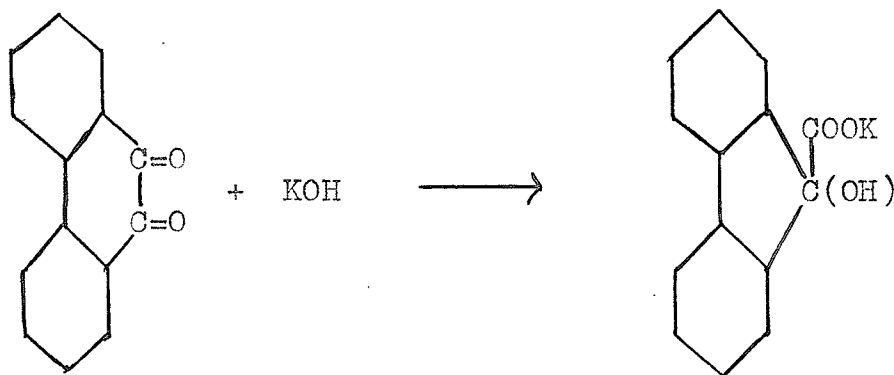
The above compound can be called:-

N,α,α-triphenyl-*β*-anil-*μ*-ketotetrahydro-oxazole.

The results of the experiment with Benzil and Phenyl-isocyanate with aluminium chloride, give support to the postulation of an intermediate product, having a chelate structure, in the Benzil-Benzilic acid rearrangement.

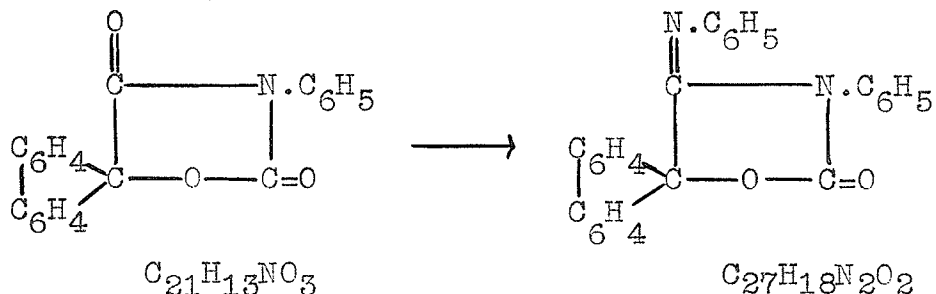
Such a compound as indicated above, might on decomposition, give Benzilic acid or a derivative of that acid.

Similarly with other diketones, such as Phenanthraquinone, which undergoes the Benzil-Benzilic acid type of rearrangement to give Oxy-fluorene-carboxylic acid.

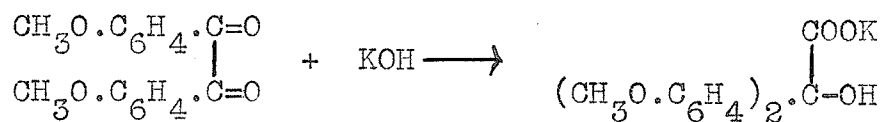


Phenanthraquinone, with Phenyl-isocyanate in the

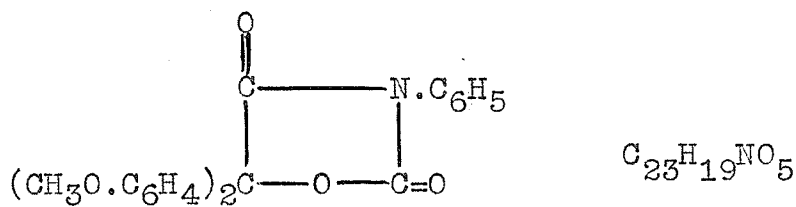
presence of aluminium chloride, would, by the same reasoning as applied to Benzil, give one of the two compounds indicated here:-



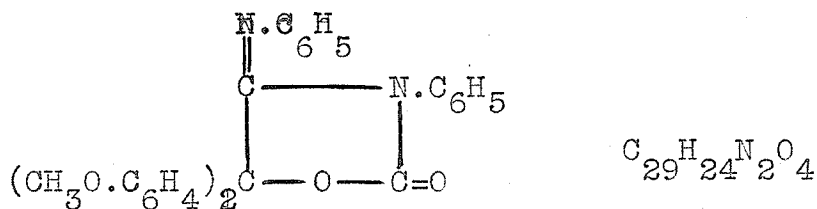
Anisil behaves like Benzil, giving Anisilic acid with aqueous or alcoholic potash:-



As with the two diketones above, Anisil would give one of the two following compounds, on treatment with Phenyl-isocyanate and aluminium chloride.



or



The following experimental work was done in an attempt to prepare any of the above suggested compounds from the different diketones with Phenyl-isocyanate using aluminium chloride; and thereby amass evidence to show that co-ordination, with the formation of a chelate structure, takes place in the Benzil-Benzilic acid Rearrangement.

As far as can be ascertained, this is the first time any attempt has been made to prepare this type of ring structure from diketones.

THE ACTION OF PHENYL-ISOCYANATE ON BENZIL
IN THE PRESENCE OF ALUMINIUM CHLORIDE.

The proportions and procedure given below have been found to give the best yield.

Benzil(210).....3.0grams(1 mol.).
Phenyl-isocyanate(119).....3.5grms(2 mol.).
Aluminium chloride(133).....1.5grams(less than one
mol. quantity.).

The first part of the preparation was carried out in the fume-cupboard, due to the very painful fumes of the Phenyl-isocyanate, and for the same reason a small Erlenmeyer flask was used at first, but it was found too difficult to remove the product, so a small(50c.cs.) beaker was subsequently used and found to serve the purpose.

The Benzil and Phenyl-isocyanate were heated in a beaker, on a water-bath, for a few minutes until the Benzil had dissolved, giving a yellow solution. The aluminium chloride was then added in small quantities at a time, with occasional stirring. There was a vigorous exothermic reaction and a very deep red liquid was obtained, which became more viscous as the aluminium chloride was added. After all the latter had been added, the beaker was heated on the water-bath until a solid was obtained. This required between one and two hours and resulted in a

deep brown solid.

On cooling, the solid was ground to a powder, and then shaken with ether in order to remove any unchanged Benzil or Phenyl-isocyanate. It was then filtered and washed with a little ether, the colour now being a light brown. The dried powder was then warmed with a very dilute hydrochloric acid solution, in which the compound was left over-night to remove aluminium chloride. When filtered and dried, the compound was dissolved in boiling alcohol, filtered while hot; on allowing to cool, a nearly white powder crystallized out. The yield was almost quantitative, three grams of Benzil giving five grams of the product. It was recrystallized once or twice from 95% alcohol until a perfectly white compound was obtained, consisting of very small needles.

THE ACTION OF PHENYL-ISOCYANATE ON BENZILIC ACID.

This reaction was first noticed by Lambling,⁵⁸ and his method is followed here.

One molecular quantity of Benzilic acid was heated in a beaker with two molecular quantities of Phenyl-isocyanate, using the water-bath. The odour of Phenyl-isocyanate disappeared after about three hours, when another molecular quantity of the isocyanate was added and the heating continued for nearly four hours. A white solid was thus obtained; when it was cold, it was

treated with ether until no more would dissolve, leaving behind insoluble carbanilide (sym-diphenylurea).

The ether solution was allowed to evaporate and yielded a viscous mass. This was then treated with alcoholic sodium hydroxide by refluxing. On cooling, a white powder separated out and this was purified by recrystallizing from boiling alcohol (95%). The product was a fine, white, crystalline powder consisting of microscopic prisms or needles. The yield was low, the chief product of the reaction being carbanilide.

The properties of the compound that was obtained from Benzil and Phenyl-isocyanate with aluminium chloride, and the properties of the compound (not the carbanilide) that was obtained from Benzilic acid and Phenyl-isocyanate are listed together below, for reasons which will become obvious.

THE PROPERTIES OF THE PRODUCTS FROM BENZIL AND
BENZILIC ACID WITH PHENYL-ISOCYANATE.

<u>From Benzil.</u>	<u>From Benzilic acid.</u>
M.P. = 180°C	M.P. = 180°C
I. Fine, white crystalline powder.	Also a fine, white crystalline powder.
II. Insoluble in water.	Insoluble in water.
III. Soluble in hot glacial acetic acid.	Soluble in hot glacial acetic acid.
IV. Soluble in pyridine.	Soluble in pyridine.
V. Slightly soluble in ether.	Slightly soluble in ether.
VI. Soluble in chloroform.	Soluble in chloroform.
VII. Soluble in benzene.	Soluble in benzene.
VIII. Soluble in warm concentrated sulphuric acid, giving a brown coloured solution.	Gave the same light-brown colour.
IX. Soluble in hot 95% alcohol, from which it crystallized on cooling.	Also recrystallized from 95% alcohol.

They both behaved in the same manner when heated alone; they melted and the liquid turned brown, fumes resembling those of Phenyl-isocyanate were given off. Conclusive evidence that the two compounds were identical, was given by taking a mixed melting point, which was found to be

180°C. After thus proving that the two compounds from the different sources were the same, any subsequent preparation of the product was made from Benzil, because the yield was found to be excellent compared to the preparation from Benzilic acid.

THE ANALYSES OF THE PRODUCT.

CARBON AND HYDROGEN.

The results of four carbon and hydrogen combustions are given.

First analysis.

Weight of combustion boat + compound	=	3.4086gms
.. alone	=	<u>3.3533</u> ..
.. .. compound	=	<u>.0553</u> ..
Weight of potash bulb after combustion	=	64.1363 ..
.. before ..	=	<u>63.9735</u> ..
Increase	=	<u>.1628</u> ..
Weight of calcium chloride tube after combustion	=	32.8298 ..
.. before ..	=	<u>32.8065</u> ..
Increase	=	<u>.0233</u> ..

$$\text{Percentage of Carbon} = \frac{12}{44} \times \frac{.1628}{.0553} \times 100 = \underline{80.3\%}$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{.0233}{.0553} \times 100 = \underline{4.7\%}$$

Second analysis.

Weight of combustion boat + compound	=	3.6692gms
.. alone	=	<u>3.5616</u> ..
.. .. compound	=	<u>.1076</u> ..
Weight of potash bulb after combustion	=	51.1242 ..
.. before ..	=	<u>50.8099</u> ..
Increase	=	<u>.3143</u> ..
Weight of calcium chloride tube after combustion	=	30.6857 ..
.. before ..	=	<u>30.6396</u> ..
Increase	=	<u>.0461</u> ..

$$\text{Percentage of Carbon} = \frac{12}{44} \times \frac{.3143}{.1076} \times 100 = \underline{79.7\%}$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{.0461}{.1076} \times 100 = \underline{4.8\%}$$

Third analysis.

Weight of combustion boat + compound	=	3.7030gms
.. alone	=	<u>3.6056</u> ..
.. .. compound	=	<u>.0974</u> ..
Weight of potash bulb after combustion	=	51.5853 ..
.. before ..	=	<u>51.2999</u> ..
Increase	=	<u>.2854</u> ..
Weight of calcium chloride tube after combustion	=	31.6652 ..
.. before ..	=	<u>31.6203</u> ..
Increase	=	<u>.0449</u> ..

$$\text{Percentage of Carbon} = \frac{12}{44} \times \frac{.2854}{.0974} \times 100 = \underline{79.9\%}$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{.0449}{.0974} \times 100 = \underline{5.1\%}$$

Fourth analysis.

Weight of combustion boat + compound = 3.6383gms

.. alone = 3.5614 ..

.. .. compound = .0769 ..

Weight of potash bulb after combustion = 60.1394..

.. before .. = 59.9144..

Increase = .2250..

Weight of calcium chloride tube after combustion = 30.6011..

.. before .. = 30.5654..

Increase = .0357..

$$\text{Percentage of Carbon} = \frac{12}{44} \times \frac{.2250}{.0769} \times 100 = \underline{79.8\%}$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{.0357}{.0769} \times 100 = \underline{5.1\%}$$

NITROGEN.

The Kjeldhal method was used to determine the percentage of nitrogen. The results of two determinations are presented:-

Strength of the sulphuric acid = .0997N

Strength of the sodium hydroxide = .1000N

1c.c. of alkali is equivalent to 1.002c.cs. of the acid.

First determination.

Weight of sample = 1.0109grams.

100c.cs. of acid required 50.0c.cs. of alkali for neutralization after distillation.

50.0c.cs. of alkali are equivalent to 50.2c.cs. of acid

$$\begin{aligned} \text{Percentage of Nitrogen} &= \frac{.014 \times (100 - 50.2) \times .0997 \times 100}{1.0109} \\ &= \underline{6.9\%} \end{aligned}$$

Second determination.

Weight of sample = .6602grams.

50c.cs. of acid required 16.8c.cs. of alkali for neutralization after distillation.

16.8c.cs. of alkali are equivalent to 16.85c.cs. of acid.

$$\begin{aligned} \text{Percentage of Nitrogen} &= \frac{.014 \times (50 - 16.85) \times .0997 \times 100}{.6602} \\ &= \underline{6.9\%} \end{aligned}$$

Mean.

Carbon = 80.3%, 79.7%, 79.9%, 79.8% = 79.92%

Hydrogen = 4.7%, 4.8%, 5.1%, 5.1% = 4.92%

Nitrogen = 6.9%, 6.9% = 6.9%

Calculated for $C_{27}H_{20}N_2O_2$ ----Carbon = 80.19%

Hydrogen = 4.95%

Nitrogen = 6.9%

The analyses agree quite well with a compound of the composition $C_{27}H_{20}N_2O_2$ and this composition also agrees with the structural compound given on p.23.

The preparation of this compound from Benzilic acid is significant, in that it proves that during the preparation of the same compound from Benzil a phenyl group must have wandered, in accordance with the conclusion reached in the theoretical discussion.

THE ACTION OF ALCOHOLIC POTASH ON THE ABOVE PRODUCT
AND THE PROPERTIES OF THE COMPOUND OBTAINED.

The compound from Benzil and Phenyl-isocyanate with aluminium chloride, was found to be extraordinary^{ly} stable. Several of the common reagents were used in an attempt to break the compound down, but only alcoholic potash was found to have any effect; and for a long time it was assumed that this reagent had no effect, as the compound obtained, as shown below, had the same melting point as the original product.

The above product was refluxed with alcoholic potash for four to five hours. The solution turned a deep brown colour. There was no indication to show the completion of any reaction, but it was found that the longer the refluxing was carried on, the better the yield.

The solution was thoroughly cooled in ice or snow and then water was added in small amounts, with shaking

after each addition, until no more precipitate would form. The precipitate, which was brownish white in colour, was filtered and dried. The filtrate was tested for any compound by extracting with ether, then extracting again with ether after making the solution acidic. There was no result in either case on evaporating the ether.

The brownish white precipitate was purified by refluxing with 95% alcohol and charcoal and filtering while hot. No solid separated out on cooling, therefore some of the alcohol was distilled off and water added until a precipitate began to form. This dilute alcohol solution was then refluxed until clear and filtered while hot. A very light-brown compound was obtained, which after re-crystallizing became a white powder.

The following listed properties show that a new compound was obtained

Before the above treatment.

After the above treatment.

M. P. = 180^o C.

M. P. = 180^o C.

Insoluble in water.

Insoluble in water.

Only soluble in hot 95% alcohol.

Soluble in hot dilute alcohol.

Slightly soluble in ether.

Readily soluble in ether.

Light brown colour with warm conc. sulphuric acid.

Reddish brown colour with warm conc. sulphuric acid.

Definite confirmation that they were not the

same was given by a mixed melting point, which was around 145^o C. Also the analyses of this compound, which hereinafter will be called the second product, proved that it was a different compound

THE ANALYSES OF THE SECOND PRODUCT.

CARBON AND HYDROGEN.

Several carbon and hydrogen combustions were performed with somewhat varying results; however, the following two seemed to be representative.

First analysis.

Weight of combustion boat + compound	=	3.7407	grms
.. alone	=	<u>3.6055</u>	..
.. .. compound	=	<u>.1352</u>	..
Weight of potash bulb after combustion	=	52.5937	..
.. before ..	=	<u>52.2188</u>	..
Increase	=	<u>.3749</u>	..
Weight of calcium chloride tube after combustion	=	36.2318	..
.. before ..	=	<u>36.1628</u>	..
Increase	=	<u>.0690</u>	..

$$\text{Percentage of Carbon} = \frac{12}{44} \times \frac{.3749}{.1352} \times 100 = \underline{75.6\%}$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{.0690}{.1352} \times 100 = \underline{5.8\%}$$

Second analysis.

Weight of combustion boat + compound	=	3.7124gms.
.. alone	=	<u>3.3481</u> ..
.. ...compound	=	<u>.1243</u> ..
Weight of potash bulb after combustion	=	53.3738 ..
.. before ..	=	<u>53.0283</u> ..
Increase	=	<u>.3455</u> ..
Weight of calcium chloride tube after combustion	=	31.4080 ..
.. before ..	=	<u>31.3426</u> ..
Increase	=	<u>.0654</u> ..

$$\text{Percentage of Carbon} = \frac{12}{44} \times \frac{.3455}{.1243} \times 100 = \underline{75.8\%}$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{.0654}{.1243} \times 100 = \underline{5.8\%}$$

NITROGEN.

The following nitrogen determinations were done by the Kjeldhal method.

Strength of the sulphuric acid = .0976N

Strength of the sodium hydroxide = .1016N

1c.c. of alkali is equivalent to 1.041c.cs. of the acid.

First determination.

Weight of sample = .4516 grams.

60c.cs. of acid required 35.75c.cs. of alkali for

neutralization after distillation.

35.75c.cs. of alkali are equivalent to 37.24c.cs. of acid.

$$\begin{aligned}\text{Percentage of Nitrogen} &= \frac{.014 \times .0976 \times (60 - 37.24) \times 100}{.4516} \\ &= \underline{7.2\%}\end{aligned}$$

Second determination.

Weight of sample = .3576 grams.

60c.cs. of acid required 40.45c.cs. of alkali for neutralization after distillation.

40.45c.cs. of alkali are equivalent to 42.11c.cs. of acid.

$$\begin{aligned}\text{Percentage of Nitrogen} &= \frac{.014 \times .0976 \times (60 - 42.11) \times 100}{.3576} \\ &= \underline{7.2\%}\end{aligned}$$

Mean Results.

Carbon = 75.7%

Hydrogen = 5.7%

Nitrogen = 7.2%

While these analyses proved that a break-down product had been obtained, it was not possible to decide what the compound was. Although the above analyses are concordant, it seemed advisable not to make any conclusive statement yet and to wait until a further study of the substance could be made.

THE ACTION OF CONCENTRATED HYDROCHLORIC ACID
ON THE SECOND PRODUCT.

The second product was heated with concentrated hydrochloric acid in a beaker on a wire gauze for about one half hour. There were indications that a reaction was taking place, in that bubbles of gas were seen and the substance turned to a light reddish brown. It was allowed to cool and then diluted with water and filtered.

The filtrate was tested in the usual way, by extracting with ether and evaporating the ether layer; then extracting the aqueous layer, after making it alkali, with ether and evaporating the ether layer. No definite result was obtained.

The reddish brown compound was washed with water and yielded a brittle brown-grey solid. This was reheated with concentrated hydrochloric acid for about fifteen minutes. After cooling, diluting and filtering, it was dried. The best recrystallizing solvent was found to be dilute alcohol. On recrystallizing once or twice, a very fine, white powder was obtained.

The Melting Point was 173°C . Insoluble in water; readily soluble in ether, and warm alcohol. Dissolved in cold concentrated sulphuric acid with a brilliant red colour (like the Benzilic acid colour), which, however, immediately disappeared on warming, the solution turning a very pale yellow and then brown on further heating.

THE ANALYSES OF THE ABOVE COMPOUND.

CARBON AND HYDROGEN.

First analysis.

Weight of combustionboat + compound = 3.4270gms.

.. alone = 3.3484 ..

.. .. compound = .0786 ..

Weight of potash bulb after combustion = 50.9800 ..

.. before .. = 50.7471 ..

Increase = .2329 ..

Weight of calcium chloride tube after combustion = 31.6964 ..

.. before .. = 31.6564 ..

Increase = .0400 ..

$$\text{Percentage of Carbon} = \frac{12}{44} \times \frac{.2329}{.0786} \times 100 = \underline{80.8\%}$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{.0400}{.0786} \times 100 = \underline{5.6\%}$$

Second analysis.

Weight of combustion boat + compound = 3.6697gms.

.. alone = 3.6052 ..

.. .. compound = .0645 ..

Weight of potash bulb after combustion = 51.1706 ..

.. before .. = 50.9800 ..

Increase = .1906 ..

Weight of calcium chloride tube after combustion = 31.7334gms.
.. before .. = 31.6997 ..
Increase = .0337 ..

$$\text{Percentage of Carbon} = \frac{12}{44} \times \frac{.1906}{.0645} \times 100 = \underline{80.5\%}$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{.0337}{.0645} \times 100 = \underline{5.8\%}$$

NITROGEN.

The Kjeldhal method was used.

Strength of the sulphuric acid = .0997N

Strength of the sodium hydroxide = .0989N

1c.c. of alkali is equivalent to .992c.cs. of the acid.

First analysis.

Weight of sample = .3115grams.

50c.cs. of acid required 40.55c.cs. of alkali for
neutralization after distillation.

40.55c.cs. of alkali are equivalent to 40.22c.cs. of acid.

$$\text{Percentage of Nitrogen} = \frac{.014 \times .0997 \times (50 - 40.22) \times 100}{.3115}$$

$$= \underline{4.4\%}$$

Second analysis.

Weight of sample = .4837grams.

50c.cs. of acid required 35.35c.cs. of alkali for neutralization after distillation.

$$\begin{aligned} \text{Percentage of Nitrogen} &= \frac{.014 \times .0997 \times (50 - 35.07) \times 100}{.4837} \\ &= \underline{4.3\%} \end{aligned}$$

Nitrogen = 4.4%

MEAN RESULTS:-

Hydrogen = 5.7%

Carbon = 80.6%

These analyses correspond to a composition of $C_{21}H_{18}N_1O_2$, this however does not give any clue as to its identity, and more research will be done before a definite statement is made about the nature of the above two breakdown products; it is not even possible to say whether the oxazole ring has been broken. It was hoped that Benzilic acid or a derivative of that acid would be obtained by the decomposition of the compound that was obtained from Benzil and Phenyl-isocyanate.

THE PREPARATION OF PHENANTHRAQUINONE.

The method of Anschutz and Schultz⁵⁹ was first tried without any success. The following procedure is very similar to the method of Oyster and Adkins,⁶⁰ which was modified by Bischoff.⁶¹

60 grams of potassium dichromate were dissolved in 300c.cs. of water, and 100c.cs. of concentrated sulphuric acid were added. This oxidizing mixture was occasionally stirred until all the dichromate had dissolved. When the mixture had been cooled, 20 grams of Phenanthraquinone were added; gradually a reaction set in, which became quite vigorous. When the reaction was over, 60 grams more of potassium dichromate were added. After allowing it to stand for a few minutes, it was then heated very gently with frequent stirring until it reached the boiling point. It was allowed to boil for a few minutes and then set aside to cool. When the mixture was cold, an equal volume of water was added with vigorous stirring and a yellow solid separated out. The mixture was then left for two or three hours.

The yellow solid was then filtered off and thoroughly washed with water. After drying, it was treated by boiling with a concentrated solution of sodium bisulphite which dissolves Phenanthraquinone. The yellow solid turned red as the Phenanthraquinone went into solution. When the

mixture had cooled slightly, it was filtered at the suction-pump, giving a greenish yellow filtrate.

The red residue was reheated with some more concentrated sodium bisulphite solution to extract any remaining Phenanthraquinone; this was then filtered, and the filtrate added to the first filtrate.

When the filtrate had cooled, an equal volume of dilute hydrochloric acid (which was found to be better than dilute sulphuric acid) was added while stirring vigorously. A yellow precipitate was formed and the whole was allowed to stand over-night. It was then filtered and washed with water. The yellow solid, when dried, was recrystallized from 95% alcohol, giving a beautiful orange coloured crystalline powder of Phenanthraquinone----M. P. = 201°C.

The yield was quite low as described by the above mentioned investigators. However, sufficient was obtained for the following experiment.

THE ACTION OF PHENYL-ISOCYANATE ON PHENANTHRAQUINONE
USING ALUMINIUM CHLORIDE, AND THE PROPERTIES
OF THE COMPOUND OBTAINED.

This experiment progressed very similarly to the one of Benzil with Phenyl-isocyanate.

Two grams of the Phenanthraquinone were heated on the water-bath with four grams of Phenyl-isocyanate for a few minutes; however the quinone did not dissolve comp-

letely. About one gram of aluminium chloride was added in small amounts at a time, with constant stirring. This produced a black, viscous liquid, which was then heated on the water-bath until a black solid was obtained.

After the mass was cool, it was ground up, giving a dark green powder. This powder was then boiled with a concentrated solution of sodium bisulphite (to remove any unchanged Phenanthraquinone), then filtered and dried.

The residue was treated with ether (for removing any Phenyl-isocyanate), filtered and allowed to dry. It was then warmed with a very dilute solution of hydrochloric acid, in which it was left over-night to remove aluminium chloride. It was then filtered and left a dark green solid. After trying various liquids, the only available method for purification was by dissolving it in hot methyl alcohol and precipitating it with water. One or two reprecipitations yielded a green powder.

This compound sublimes at 174°C . It is soluble in acetone, hot 95% alcohol and hot methyl alcohol. It is insoluble in water, benzene, glacial acetic acid and petroleum ether. It dissolved in cold concentrated sulphuric acid giving a beautiful blue-violet colour.

THE ANALYSES OF THE ABOVE COMPOUND.

CARBON AND HYDROGEN.

First analysis.

Weight of combustion boat + compound	=	3.4161gms	
.. alone	=	<u>3.3484</u>	..
.. .. compound	=	<u>.0677</u>	..
Weight of potash bulb after combustion	=	51.3572	..
.. before ..	=	<u>51.1693</u>	..
Increase	=	<u>.1879</u>	..
Weight of calcium chloride tube after combustion	=	31.7646	..
.. before ..	=	<u>31.7340</u>	..
Increase	=	<u>.0306</u>	..

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{.1879}{.0677} \times 100 = \underline{75.6\%}$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{.0306}{.0677} \times 100 = \underline{5.1\%}$$

Second analysis.

Weight of combustion boat + compound	=	3.7180gms	
.. alone	=	<u>3.6052</u>	..
.. .. compound	=	<u>.1128</u>	..
Weight of potash bulb after combustion	=	51.6446	..
.. before ..	=	<u>51.3568</u>	..
Increase	=	<u>.2878</u>	..

Weight of calcium chloride tube after combustion = 31.8196gms
.. before .. = 31.7646 ..
Increase = .0550 ..

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{.2878}{.1128} \times 100 = \underline{75.3\%}$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{.0550}{.1128} \times 100 = \underline{5.4\%}$$

NITROGEN.

The Kjeldhal method was used.

Strength of the sulphuric acid = .0976N

Strength of the sodium hydroxide = .1012N

1c.c. of alkali is equivalent to 1.037c.cs. of the acid.

First analysis.

Weight of sample = .4522grams.

50c.cs. of acid required 13.4c.cs. of alkali for
neutralization after distillation.

13.4c.cs. of alkali are equivalent to 13.9c.cs. of acid.

$$\begin{aligned} \text{Percentage of Nitrogen} &= \frac{.014 \times .0976 \times (50 - 13.9) \times 100}{.4522} \\ &= \underline{10.9\%} \end{aligned}$$

Second analysis.

Weight of sample = .3842grams.

50c.cs. of acid required 18.2c.cs. of alkali for
neutralization after distillation.

18.2c.cs. of alkali are equivalent to 18.9c.cs. of acid.

$$\text{Percentage of Nitrogen} = \frac{.014 \times .0976 \times (50 - 18.9) \times 100}{.3842}$$

$$= \underline{11.1\%}$$

Assuming that the same type of compound is formed as with Benzil and Phenyl-isocyanate, then the percentages would be(see p.24):-

	<u>C₂₇H₁₈N₂O₂</u>	<u>C₂₁H₁₃NO₃</u>	<u>Experimental.</u>
Carbon	80.6%	77.1%	75.45%
Hydrogen	4.5%	3.9%	5.2%
Nitrogen	7.0%	4.3%	11.0%

Thus the compound obtained from Phenanthraquinone and Phenyl-isocyanate, according to the above analyses, has neither of the two structures mentioned. The analyses point to a formula C₂₆H₂₀N₃O₂, but further investigation is desirable before any definite statement is made. The percentage of nitrogen observed seems very high.

This compound was also attacked by alcoholic potash, on refluxing, but the yield was not sufficient to permit any analyses.

THE PREPARATION OF ANISOIN.

The following method was first described by Bosler.⁶²

Ten grams of Anisaldehyde were refluxed with slightly less than two grams of sodium cyanide (dissolved in eight grams of water) and twelve grams of 95% alcohol. After two hours another equal amount of sodium cyanide was added and the boiling (refluxing) continued for nearly two hours.

Stierlin⁶³ suggested that the liquid should be shaken for about fifteen minutes as the liquid cooled. The best procedure was found to be to shake the liquid well and then leave ^{it} over-night. The reddish coloured crystals that were thus obtained were filtered, and on shaking with ether, the colour disappeared, leaving a yellowish powder. When dry, the powder was recrystallized from dilute alcohol. The yield was about four grams of yellow Anisoin with M. P. = 113°C.

THE PREPARATION OF ANISIL.

Two methods of oxidizing the Anisoin were tried. Using nitric acid, as in the formation of Benzil from Benzoin, was quick but did not give as good a yield as the following method, which is, however, more complicated.

It is the method of Irvine and Moodie.⁶⁴

The Anisoin was boiled for nearly three hours, with the calculated amount of alkaline potassium permanganate. A beaker was used on a wire gauze. The dark-coloured mixture that was obtained, was filtered, washed with water and dried.

To extract the Anisil, the dry residue was boiled with ether using a reflux condenser. The warm ether solution was quickly filtered and on cooling, the Anisil crystallized out. It was recrystallized from 95% alcohol and yielded yellow needles melting at 132^o C.

THE ACTION OF PHENYL-ISOCYANATE ON ANISIL
IN THE PRESENCE OF ALUMINIUM CHLORIDE.

The procedure followed here is the same as the method described for Benzil with Phenyl-isocyanate.

The Anisil was heated with the Phenyl-isocyanate on the water-bath, until it had dissolved. The aluminium chloride was then added in small quantities at a time; the viscous liquid that resulted was brownish red. It was heated on the water-bath until a solid was obtained.

This black solid was ground up when cold and yielded a very dark yellow compound. This was treated with ether to remove any unchanged Anisil and Phenyl-isocyanate. After filtering, the compound was warmed with a very dilute solution of hydrochloric acid, in which it was left overnight to remove aluminium chloride.

The solid was filtered and dried. On recrystallizing from 95% alcohol a fine, white compound was obtained,

having a melting point of 177.5°C .

THE ANALYSES OF THE ABOVE COMPOUND.

CARBON AND HYDROGEN.

First analysis.

Weight of combustion boat + compound	=	3.5400gms
.. alone	=	<u>3.3482</u> ..
.. .. compound	=	<u>.1918</u> ..
Weight of potash bulb after combustion	=	50.8968 ..
.. before ..	=	<u>50.4357</u> ..
Increase	=	<u>.4611</u> ..
Weight of calcium chloride tube after combustion	=	30.7870 ..
.. before ..	=	<u>30.6952</u> ..
Increase	=	<u>.0918</u> ..

$$\text{Percentage of Carbon} = \frac{12}{44} \times \frac{.4611}{.1918} \times 100 = \underline{71.4\%}$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{.0918}{.1918} \times 100 = \underline{5.3\%}$$

Second analysis.

Weight of combustion boat + compound	=	3.7038gms
.. alone	=	<u>3.5558</u> ..
.. .. compound	=	<u>.1480</u> ..

Weight of potash bulb after combustion = 50.9682gms
.. .. before .. = 50.5711 ..
Increase = .3971 ..

Weight of calcium chloride tube after combustion = 31.5632 ..
.. .. before .. = 31.4968 ..
Increase = .0664 ..

$$\text{Percentage of Carbon} = \frac{12}{44} \times \frac{.3971}{.1480} \times 100 = \underline{71.6\%}$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{.0664}{.1480} \times 100 = \underline{4.9\%}$$

NITROGEN.

The Kjeldhal method was used. There was only enough sample to do one determination(.4600grams).

Strength of the sulphuric acid = .0997N

Strength of the sodium hydroxide = .0984N

1c.c. of alkali is equivalent to .987c.cs. of the acid.

50c.cs. of acid required 32.2c.cs. of alkali for neutralization after distillation.

32.2c.cs. of alkali are equivalent to 31.8c.cs. of acid.

$$\begin{aligned} \text{Percentage of Nitrogen} &= \frac{.014 \times .0997 \times (50 - 31.8) \times 100}{.4600} \\ &= \underline{5.5\%} \end{aligned}$$

On comparing these results with the suggested compounds given on p.24, as tabulated below,

	<u>C₂₃H₁₉NO₅</u>	<u>C₂₉H₂₄N₂O₄</u>	<u>Experimental.</u>
Carbon	70.95%	75.00%	71.5%
Hydrogen	4.8%	5.2%	5.1%
Nitrogen	3.6%	6.0%	5.5%

The reason for the investigation of the behaviour of Anisil with Phenyl-isocyanate was that it was hoped to obtain a compound similar to that of Benzil with Phenyl-isocyanate, that would break down easily. However, the investigation had to stop with only the above results, as the supply of Anisaldehyde ran out. Until further work can be done on the compound from Anisil, there is no point in stating anything as to its composition.

SUMMARY.

The different theories that have been advanced to explain the Benzil-Benzilic acid Rearrangement have been discussed, and also the reasons why they were discarded.

A tentative theory has been presented, based on the Electrochemical(Electronic) Theory, postulating that co-ordination takes place with the formation of a chelate structure, during the rearrangement.

Compounds have been obtained from Benzil, Phenanthraquinone and Anisil with Phenyl-isocyanate, in the presence of aluminium chloride.

The analyses of the compound from Benzil agree perfectly with what was to be expected from the theory advanced to explain the Benzil-Benzilic acid Rearrangement, and thus may be offered as evidence that this rearrangement takes place by co-ordination with the formation of a chelate structure as suggested.

As in the case of the break-down products of the compound from Benzil and Phenyl-isocyanate, so in the case of the two compounds from Phenanthraquinone and Anisil, further investigation will be done before any conclusions are reached. The results given in these two cases only show that Phenyl-isocyanate reacts readily with the diketones and the compounds obtained are very stable.

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