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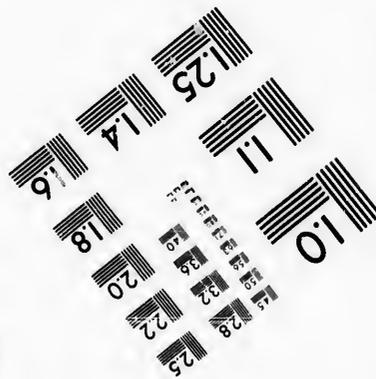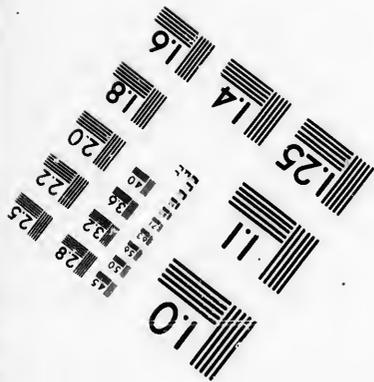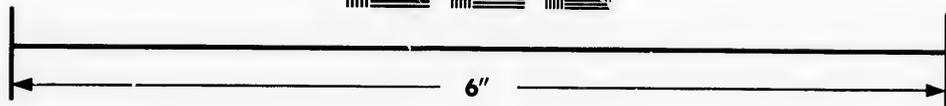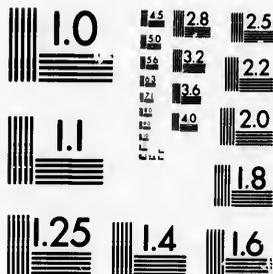
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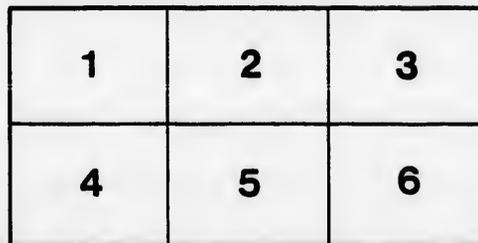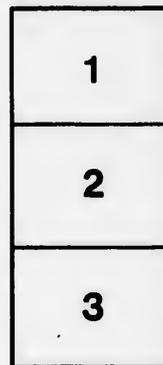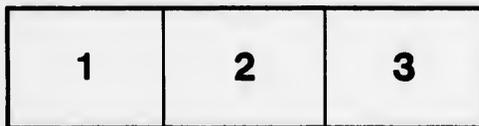
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THE TAUTOMERISM OF

Oxymethylene and Formyl Compounds

By CHAS. G. L. WOLF, B.A., M.D. 1894

Demonstrator of Practical Chemistry, McGill University

V.—*The Tautomerism of Oxymethylene and Formyl Compounds.*

By CHAS. G. L. WOLF, B.A., M.D.

Demonstrator of Practical Chemistry, McGill University.

(Communicated by Dr. Ruttan and read May 25, 1898.)

Of the different kinds of isomerism which are found in organic complexes, that perhaps which has excited the greatest amount of interest in the last five years has been *Tautomeric.*

Tautomerism may be defined as the property which metameric bodies may possess of reciprocal transformation, the change being due to a certain part of the molecule being labile, and under different conditions, of having a tendency to select one or other part of the complex as its place of junction.

The word Tautomerism, derived from the Greek $\tau\alpha\upsilon\tau\sigma\varsigma$, *the same,* is not perhaps the most suitable name etymologically that could be chosen, but as it is the name which has been longest in use, it is still retained to denote this property. Of the other names which have been suggested since the publication of Laar's papers, the more important are : Desmotropism, Merotropism, Pseudomerism and Tropomerism.

Desmotropism, suggested by Jacobson ($\Delta\epsilon\sigma\mu\sigma\varsigma$) ;

Merotropism, by Michael (*$M\epsilon\rho\sigma\varsigma$*);

Pseudomerism, by Laar ($\psi\epsilon\upsilon\delta\eta\varsigma$) ;

although having in special cases some significance, are scarcely to be commended, because of the implication that one of the tautomeric compounds is the more stable. In the case of ethyl formyl phenyl acetate, the stability of the two isomers is practically alike, so that, in this case, a definition of this kind does not exactly apply.

Claisen has made the suggestion that the word Tropomerism (*$T\rho\epsilon\phi\epsilon\iota\nu$*) should be used, but he did not insist upon it, on the ground that there are already too many designations for the property.

The first important contribution to the subject was that of Conrad Laar, who in his first paper, and especially in his second, attempted very successfully to give a classification of those molecular arrangements which would be capable of existing in isomeric modifications dependent on the shifting of a part of the molecule from one position to another. He divides tautomers according to the number of atoms over which the labile part would move.

The first classification divides the groups into two : (1) Dyads or artiads, and (2) triads or perissads. From the combination of these one is able to obtain still more complex groups capable of tautomerism.

The dyad type is naturally a restricted one, and consists of two polyvalent atoms bound together with more than a single bond, to the one or other of which the labile hydrogen or other group may be attached. Hydrocyanic acid is an example of this class.   The formula can be represented in two ways :

$$N \atop \underset{\text{Hydrocyanic acid.}}{\overset{\text{\textbar\textbar\textbar}}{C \cdot H}} \qquad\qquad \underset{\text{Isohydrocyanic acid,}}{\overset{N-H}{\underset{C}{\text{\textbar\textbar}}}}$$

and for the methyl derivatives :

$$N \atop \underset{\text{Methylcyanide.}}{\overset{\text{\textbar\textbar\textbar}}{C \cdot CH_3}} \qquad\qquad \underset{\text{Methyl isocyanide.}}{\overset{N \cdot CH_3}{\underset{C}{\text{\textbar\textbar}}}}$$

Nef here assumes a divalent carbon for the formula of hydrocyanic acid, because of the great addition capacity of potassium cyanide.

A second dyad type is that to which the benzol sulphinic acids belong.   They contain a grouping which may react as

$$\underset{O=S-Ph}{\overset{O \cdot H}{|}} \qquad or \qquad O=\underset{Ph}{\overset{O}{\underset{|}{\overset{||}{S}H}}}$$
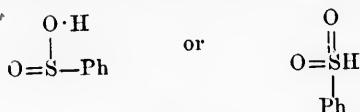
The sodium salts of this acid react with alkyl iodides according to the first formula ; the ethyl ester of carbonic acid gives, on the other hand, the sulphinic esters corresponding to the second type.

The triads consist of three polyvalent atoms joined together.   The middle atom must be at least trivalent, and the other two divalent.

Laar divides the triads into six classes.   It would be beyond the limits of this paper to go into a detailed description of the different forms in which triads present themselves, except in so far as the oxymethylene compounds are considered.   The following table gives a list of the combinations in which the elements group themselves :

TRIAD TYPES—I.

CLASS I . . . . GROUP I . . . . $-N-\overset{|}{\underset{H}{C}}=O$ and $-N=\overset{C-O}{\underset{H}{|}}$

GROUP II . . . . . $-N-\overset{|}{\underset{H}{C}}=S$ and $-N=\overset{C-S}{\underset{H}{|}}$

GROUP III . . . . . $-N-\underset{H}{\overset{|}{C}}=N-$ and $-N=\overset{C-N}{\underset{H}{|}}$

GROUP IV..... $\overset{|}{\underset{H}{S}}-\overset{|}{C}=O$ and $S=\overset{|}{C}-\overset{|}{\underset{H}{O}}$

GROUP V...... $-\overset{|}{\underset{H}{N}}-\overset{|}{C}=N-\overset{|}{C}=O$ and $-N=\overset{|}{C}-N=\overset{|}{C}-\overset{|}{\underset{H}{O}}$

CLASS II..........GROUP I....... $O-\overset{|}{\underset{H}{C}}=\overset{|}{C}$ and $O=\overset{|}{C}-\overset{|}{\underset{H}{C}}-$

Mixed and terminal carbon atoms.

GROUP II... .. $-\overset{|}{\underset{H}{N}}-\overset{|}{C}=\overset{|}{C}$ and $-N=\overset{|}{C}-\overset{|}{\underset{H}{C}}-$

GROUP III..... $H-S-\overset{|}{C}=\overset{|}{C}-$ and $S=\overset{|}{C}-\overset{|}{\underset{H}{C}}-$

PERISSAD ..... $O-\overset{|}{\underset{H}{C}}=\overset{|}{C}-\overset{|}{C}=N-$ and $O=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-\overset{|}{\underset{H}{N}}-$

CLASS III.........GROUP I....... $-\overset{|}{\underset{H}{C}}-\overset{|}{C}=\overset{|}{C}-$ and $\overset{|}{C}=\overset{|}{C}-\overset{|}{\underset{H}{C}}-$

Unsaturated hydrocarbon chain.

CLASS IV.........GROUP I... ... $O-N=N-$ and $O=N-N-$
$\overset{|}{H}$ $\overset{|}{H}$

Chains without carbon.

GROUP II...... $-\overset{|}{\underset{H}{N}}-N=N-$ and $-N=N-\overset{|}{\underset{H}{N}}-$

CLASS V..........GROUP I....... $O-N=\overset{|}{C}-$ and $O=N-\overset{|}{C}-$
$\overset{|}{H}$ $\overset{|}{H}$

Middle nitrogen and terminal carbon atoms.

GROUP II...... $-N-\overset{|}{N}=\overset{|}{C}-$ and $-N=N-\overset{|}{C}-$
$\overset{|}{H}$ $\overset{|}{H}$

CLASS VI........................ $-\overset{|}{\underset{H}{C}}-N=\overset{|}{C}-$ and $-\overset{|}{C}=N-\overset{|}{\underset{H}{C}}-$

Two carbon atoms bound together by nitrogen.

The oxymethylene compounds belong to Laar's second class of triads, in which besides a middle carbon atom, one has at one end another atom of the same kind. To this class belong the ketones, aldehydes and the phenols, which may be represented by the tautomeric groups.

$=CH$ $=C$
$|$ $||$
$-C=O$ $-C-OH$

Keto or aldo form.   Enol form.
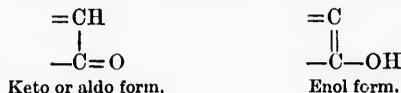
Although Polok and Thummel have attempted to prove that the tautomer of acetaldehyde, the simplest member of the group except for maldehyde, exists, it is somewhat doubtful if such is the case.

The alkyl derivatives corresponding to these compounds are however known, for example :

$$H_2C \cdot C_2H_5$$
$$| $$
$$H \quad C=O$$
Butyric aldehyde.

$$H_2C$$
$$||$$
$$HC \cdot OC_2H_5$$
Vinyl Ethyl Ether.

$$H_2C \cdot C_2H_5$$
$$|$$
$$CH_3 \cdot C=O$$
Methyl propyl ketone.

$$CH_2$$
$$|$$
$$CH_3C—OC_2H_5$$
Isopropenyl ethyl ether.
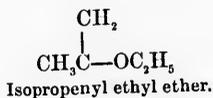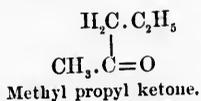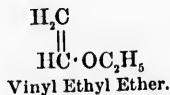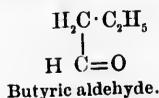
Isomerides are more difficult to obtain in these cases where the labile part is a hydrogen atom, for the presence of a difficultly movable group such as ethyl, by increasing the stability of the molecule, favours the formation of two compounds of tautomeric structure. That the ethyl group itself can be labile is best shown by Claisen's experiment of long continued heating of isoacetophenon phenyl ether, which changes into phenyl propyl ketone. The ketone, as one would expect, is the more stable compound.

The extreme mobility of the hydrogen, as compared with complex groups in cases of this kind, is not to be wondered at, when one sees that it plays the same part in dissociation processes in solution.

The most important compound which has displayed tautomeric phenomena is ethyl aceto acetate, to which since its simultaneous discovery in 1863 by Geuther, and Frankland and Duppa, two formulæ have been ascribed, which are known respectively as the Geuther and Frankland formulæ. Geuther viewed it as a β oxycrotonic ester, having the structure

$$CH_3 \cdot C=CH \cdot COOC_2H_5$$
$$|$$
$$OH$$
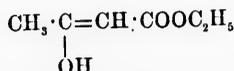
while Frankland's formula was that of the acetyl derivative of acetic ester,

$$CH_3CO \cdot CH_2COOC_2H_5$$

This ester, on account of the numerous syntheses to which it has been applied, had been the subject of the most thorough study. Many of the derivatives of this most interesting compound are to be described as belonging to the first formula. On the other hand, the physical properties of the compound are only concordant with the second.

It is therefore necessary to assume if one wishes to bring the two formulæ into concordance, that although the ester itself is the carboxylic ester of acetone, it is capable of reacting as its tautomer, giving derivatives of the oxycrotonic ester.

Chemical reactions used alone for proving the constitution of a compound of this kind, are apt to lead to difficulties which cannot be explained away by any hard and fast rule.

To the second class of Laar belong the ketones, aldehydes and phenols, and also the acids and their esters.

$$=CH \qquad =CH \qquad =C \qquad =C$$
$$HO-C=O \qquad C_2H_5O\cdot C=O \qquad HO-C-OH \qquad C_2H_5O\cdot C-OH$$
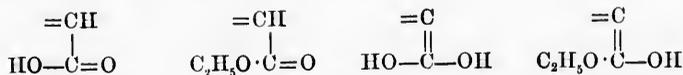
The possibility is therefore present that ethyl malonate may act in a tautomeric sense, and, indeed, Michael has suggested that the sodium derivative of malonic ester may be represented by the formula,

$$\begin{array}{c} COOC_2H_5 \\ / \\ HC\cdot O\ Na \\ \backslash \\ COC_2H_5 \end{array}$$
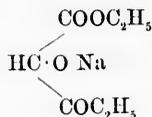
whereas the free ester certainly has the formula,

$$\begin{array}{c} COOC_2H_5 \\ / \\ HCH \\ \backslash \\ COOC_2H_5 \end{array}$$
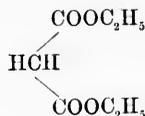
The closely allied dicarboxyglutaconic ester, on the other hand, appears to have the enol formula in the free state, and would possess the second of the following two constitutions :

I
$$\begin{array}{c} \quad\quad COOC_2H_5 \\ C< \\ \quad\quad COOC_2H_5 \\ \| \\ CH \\ | \\ HC< \begin{array}{l} COOC_2H_5 \\ COOC_2H_5 \end{array} \end{array}$$

II
$$\begin{array}{c} \quad\quad COOC_2H_5 \\ C< \\ \quad\quad COOC_2H_5 \\ \| \\ CH \\ | \\ C\cdot COOC_2H_5 \\ \| \\ C\cdot OH \\ \backslash \\ OC_2H_5 \end{array}$$
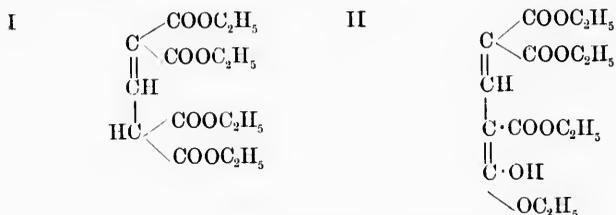
This would be an example which, compared with acetic ester, would tend to prove the law of Claisen, that the enol form is the more likely

to be produced the more negative the groups combined to the methene group in question. Hence,

Dicarboxyglutaconic ester.   Acetoacetic ester.
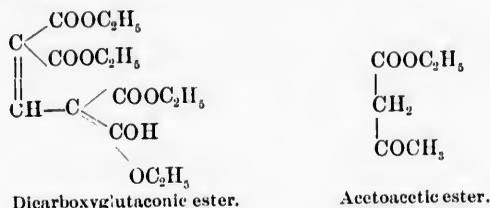
The grounds for this assumption are the formation of a lactone, the ethoxypyrone diearboxylic ester on heating (presupposing the presence of a hydroxyl group), and also the ferric chloride reaction and the absorption capacity for electrical oscillations of high frequency, the significance of both of which will be explained later.

The investigation of tautomeric compounds is thus confined to substances which have a double bond and a hydrogen atom in a certain position relative to this bond. Many substances have been obtained which are tautomeric in the sense that certain derivatives obtained by chemical reactions, and which should have been identical, have been found to differ. Such, for instance, to take a simple example, is benzamide ; this substance, and other acid amides, as Tafel and Enoch show act with alkyl iodides according to two formulæ, giving in the one case oxygen derivatives or oximido esters ; in the other true nitrogen esters, which may be represented by the following :

$$C_6H_5-C{<}^{OC_2H_5}_{NH} \quad \text{and} \quad C_6H_5-C{<}^{O}_{NHC_2H_5}$$
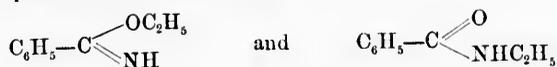
Here one has a compound which, like ethyl acetoacetate, is homogeneous, but whose silver salt reacts in a different manner from its sodium salt, with the same reagent.

Benzamide is a representative of compounds which far outnumber the second class of isomerides, which is more directly connected with this paper.

These are the compounds which not only yield tautomeric derivatives, but can themselves exist in two forms which can be represented by tautomeric formulæ.

On account of the extreme lability of the hydrogen atom, these isomers are much more difficult to obtain. The following table will give a *résumé* of these compounds :

ACETYLDIBENZOYLMETHANE. Claisen, Ann. d. Chem., 291, 25.	$C{<}^{C\,(OH).CH_3}_{CO.C_6H_5}_{CO.C_6H_5}$ or $HC{<}^{CO.CH_3}_{CO.C_6H_5}_{CO.C_6H_5}$ a β Solid, M.P., 80—85°. Solid, M.P., 107—110°.

TRIBENZOYLMETHANE. Claisen, ebenda.	$C \big\langle \begin{matrix} C\,(OH).C_6H_5 \\ CO.C_6H_5 \\ CO.C_6H_5 \end{matrix}$ or $CH \big\langle \begin{matrix} CO.C_6H_5 \\ CO.C_6H_5 \\ CO.C_6H_5 \end{matrix}$ a $\qquad\qquad$ β Solid (before melting) Solid, M.P., 222—226°. changing to β.
MESITYLOXYDOXALESTER. (——Methyl ester and free acid). Claisen, ebenda.	$CO.\ CH:C\,(CH_3)_2$ $\overset{\mid}{CH}:C\,(OH).\ COOC_2H_5$ a M.P., 21—22°. or $CO.\ CH:C\,(CH_3)_2$ $\overset{\mid}{CH_2}.\ CO.\ COOC_2H_5$ β Solid, M.P., 59—60°. B.P., 260—268°.
FORMYLPHENYLACETIC ESTER. Wislicenus, Ann d. Chem. 291, 147	$\begin{matrix} C_6H_5 \\ COOC_2H_5 \end{matrix}\Big\rangle C:CH\,(OH)$ a Fluid, B.P., 135° b. 15 mm. or $\begin{matrix} C_6H_5 \\ COOC_2H_5 \end{matrix}\Big\rangle CH.CHO$ β Solid, M.P. ca. 70°.
DIOXYPYRIDINDICARBOXYLIC ESTER. Guthzeit, Ann. d. Chem. 285, 35. Ber. d. deutsch. Chem. Ges. 26, 2795.	$COOC_2H_5$ $CH \big\langle \begin{matrix} \overset{\mid}{C}:C\,(OH) \\ C-C\,(OH) \end{matrix} \big\rangle N$ $COOC_2H_5$ Solid, M.P., 199° or $COOC_2H_5$ $CH \big\langle \begin{matrix} \overset{\mid}{C}H-CO \\ C - CO \end{matrix} \big\rangle NH$ $\overset{\mid}{C}OOC_2H_5$ Solid, M.P., 179°
DIACETYLSUCCINIC ESTER. Similarly, Dibenzoylsuccinic ester. Knorr, Ann. d. Chem. 293, 70.	$CH_3.C\,(OH):C.COOC_2H_5$ $CH_3.C\,(OH):\overset{\mid}{C}.COOC_2H_5$ a Fluid. or $CH_3.CO.CH.COOC_2H_5$ $CH_3.CO.\overset{\mid}{C}H.COOC_2H_5$ Solid $\begin{cases} \beta \text{ M.P., } 88°. \\ \gamma \text{ M.P., } 68°. \end{cases}$

Ester of J. Wislicenus. Hagemann and Callenbach. Ber. d. deutsch. chem. Ges. 30, 639.	(1) $CH_3.C$ with $CH.C(OH)$ and $CH_2 . CH_2$ forming $C.COOC_2H_5$ (2) $CH_3.C$ with $CH -- CO$ and $CH_2 . CH_2$ forming $CH.COOC_2H_5$ (1) Fluid, B.P., 150—152° at 22 mm. (2) Fluid, B.P., 148—152° at 22 mm.
Dibenzoylmethane. Wislicenus, Löwenheim & Wells. Ber. der säehs. Akad. (Sitzung v.) 1, March, 1897.	CH with $C(OH).C_6H_5$ and $CO.C_6H_5$; CH_2 with $CO.C_6H_5$ and $CO.C_6H_5$ Solid, M.P., 77·5—78°. Solid, M.P., 77·5—78°.
Phenylnitromethane. Hantzsch & Schultze. Berd. d. deutsch. Ges. 29, 699, 2251. '' Rec. trav. ehim. 1 .56, 365.	$C_6H_5. CH=N$ with O and OH $C_6H_5. CH_2. NO_2$ (Iso-Ph.) Solid, M.P., 84°. Fluid.

It will now be necessary to go into the grounds for assuming that the differences in the compounds are due to tautomeric change and not to any other form of isomerism which plays a part in organic chemistry.

The proofs may be divided into two sections ; physical and chemical.

Of the two classes, that one which is the more likely to give certain results is the first, for it assumes that in the process of physical examination no change will take place in the compounds under investigation. In the case of chemical reaction, one can never be certain that substances, especially those which are susceptible to change, will not undergo under the influence of heat, or cold, solvents, foreign substances in proximity, etc., changes which will render the results, if not valueless, at least uncertain.

The physical methods which lend themselves to the constitutive examination of substances are few in number, but they have in this direction been exceedingly useful. They are :

1. The determination of the molecular refraction.
2. The determination of the molecular magnetic rotation.
3. The determination of the molecular volume.
4. The selective absorption.
5. The absorption for electric oscillations.

The first three of these methods are mainly the result of the representative work of Brühl, W. H. Perkin, sr., and of I. Traube. They are in contradistinction to the latter two, quantitative, and admit in many cases of an accurate judgment being made of the constitution of a compound. They rest on the assumption that the molecular properties of organic substances are the sum of their atomic functions. The spectrometric investigations of Brühl, who has determined the molecular refractions of

a very great number of substances using the formula of Lorenz and Lorentz, and the numbers of Conrady, $R = \dfrac{(n^2-1)\,w}{(n^2+2)\,d}$. Where R is the molecular refraction, n the refractive index, and d the density, and w the molecular weight, show that in substances of the formyl and oxymethylene types, the former possess, in consequence of the lack of a double bond, a much lower molecular refraction that could be accounted for by any errors of observation. The dispersion would also appear to stand in close relation with the constitution of these substances.

Perkin's work on the influence of the constitution of substances on the rotation which polarized light undergoes when passing through layers of substances in a strong magnetic field, has led to like results.

The selective absorption of substances has been another property which has been made use of for determining the presence or absence of hydroxyl groups in substances suspected to contain them, and the recent extremely interesting results of Spring would tend to show that there is a definite relation between this group and the colour of liquids observed in long layers.

The investigation of the molecular solution volume which is dependent on the determination of the specific gravity of solutions, is also a most useful method for the differentiation of isomers of the tautomeric type, and as Wislicenus remarks, it would be of much value, considering the behaviour of these compounds in solution, to determine quantitatively by this method, to what extent the dissociating capacity affects the compound, and, perhaps, although open to doubt, one might obtain results agreeing to some extent with those obtained by colorimetric means.

The last method is that of Drude, who in the course of an investigation into the dielectric constants of organic bodies, has shown that compounds containing hydroxyl display an anomalous absorption for electric oscillations of a definite period, but of high frequency.

The writer has had the advantage of examining some of the substances which are described in this paper in an apparatus constructed by Prof. Drude, and has been able to confirm results obtained chemically by this means.

The method, which is a beautiful qualitative one, possesses the advantage of giving immediate negative or positive results, of being easily used, and of requiring but small quantities of the substance under examination. The original papers will be found in Wiedemann's Annalen, 60, 500, and in the Berichte der deutschen chemischen Gesellschaft, 30, 940.

In contradistinction to the methods above described are the chemical, which, although giving results of the utmost value, are not attended with the same surety.

The reagents which are principally concerned in this paper are those which will differentiate the formyl group :

$$
\begin{array}{c}
HC{=}O \\
| \\
HC{=}
\end{array}
$$

from the oxymethylene group,

$$
\begin{array}{c}
HC{-}OH \\
|| \\
HC{-}
\end{array}
$$

or, in other words, reagents reacting on hydroxyl, but not on the aldo group. Of these, the first is acetic anhydride. This reacts, as is well known, with hydroxyl compounds, giving an acetate according to the general formula :

$$\equiv C.OH + (C_2H_3O_2)O = \ \equiv C.OC_2H_3O_2 + CH_3COOH.$$

The demand that this method makes for a temperature exceeding 100° is sufficient to render it untrustworthy, and, as with formyl phenyl acetic ester and oxymethylene phenylacetic ester, as with most of the compounds on which it has been tried, identical acetates have been obtained.

Hydroxylamine and phenylhydrazine have been used to determine the presence of aldehydes or of ketones. That these are of smaller value than one would be led to expect at first sight will be shown in the experimental part of this paper, and this is undoubtedly due to the formation from the two tautomers of identical addition products, which on losing water give the same derivative. There is, however, a reagent, which, unlike the amines, seems to have the selective power sought for, and this is phenyl isocyanate or carbanil, suggested by Goldschmidt, and investigated further by Michael, which combines with hydroxyl, amide and imide groups, giving respectively urethanes and substituted ureas.

$$\equiv C . OH + C_6H_5NCO= \ \equiv CO . CONHC_6H_5$$

$$\equiv C . NH_2 + C_6H_5NCO= \ \equiv C . NH CONHC_6H_5$$
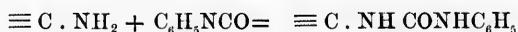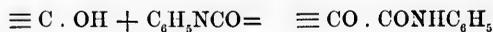
With ketones, however, the substance does not react This has proved to be the case with oxymethylene phenylacetic ester, which gives the corresponding carbanilic acid ester, whereas the ketone compound does not form an additive product with this substance.

The most general reagent which has been used for the recognition of hydroxyl in groups closely allied to the oxymethylene combination, has been ferric chloride. This test, which is dependent on the formation of

a red or blue colour with an aqueous solution of ferric chloride differentiates the group.

$$-CO - CH - CO- \quad \text{and} \quad - CO.CH . COOC_2H_5$$
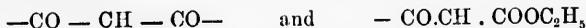
from their hydroxyl tautomers, and hence is displayed by β diketones and β ketonic esters as aceto acetic ester. This colour is due to an unstable compound, of which that of Claisen has been analysed. And in the last journal of the Chemical Society, Morrel and Crofts report the isolation of a similar compound from ketophenylparaconic methyl ester by the action of an anhydrous ethereal solution of ferric chloride.

That the reaction is due to the enol form and not to that of the aldo of keto modification, is shown by the fact that phenols and substances such as salicylic ester display an analogous behaviour.

This agrees with the results obtained by the treatment of the two forms of formylphenylacetic ester with ferric chloride. That form whose physical properties, molecular refraction, rotation, etc., point to its possessing the enol formula, gives an intense coloration with this reagent. On the other hand, that having the formyl configuration does not react except after long standing, during which time, owing to the catalytic action of the electrolyte, a tautomeric transformation has taken place.

One of the most interesting applications of this reaction will be spoken of in the experimental part of this paper. It is the use of a colorimetric method to determine to what extent the tendency towards enolization or aldolization is exerted in media which have different dissociation capacities, and although those experiments have not yielded strictly quantitative results, the information they have afforded has thrown much light on the tendency of the substances to establish an equilibrium of the two isomers more or less rapidly, according to the nature of the solvents.

The method briefly described is this: A weighed quantity of substance under examination is dissolved in a definite amount of the various solvents, $e.g.$, methyl alcohol, ethyl alcohol, benzol, ether or chloroform, and after being allowed to stand for a certain time, aliquot parts are diluted with alcohol, a single drop of ferric chloride solution added, and the colour compared in the very convenient colorimeter of Duboscq. They are also compared with a fresh alcoholic solution of the compound. According as the substance has been changed to the enol, or to the aldol form, one gets a deepening of the colour or the reverse.

It has been shown by Wislicenus, in the case of oxymethylene phenyl acetic ester, that the α form tends to become converted to the keto derivative, shown by a lessening of the intensity of the colour, while in the case of the β compound, a solution after standing has not the same intensity of colour as that observed with a fresh solution.

Belonging to the same class as the ferric chloride reaction are the compounds which are formed by substances containing the enol complex with the alkali metals, and with copper and silver. All those substances containing a labile hydrogen atom, with the exception of Laar's class III., give compounds with the metals.

It is now of interest to know how far the metals possess the same capacity as the hydrogen to give tautomeric compounds. It is well known that the dissociation constants of weak organic acids are not so large as these of the corresponding salts. It would, therefore, be expected that on account of the extreme lability of these atoms, the isolation of tautomers would be much more difficult. As yet, isomers of this kind have been obtained in relatively few cases, one of which is to be found with oxymethylene phenyl acetic ester.

The determination of the constitution is also much more complex, as there are at present no physical methods to guide as in the case of the original substances.

When the α form of oxymethylene phenyl acetic ester is dissolved in ether, and the mixture treated with metallic sodium, one obtains a sodium derivative which must be regarded as

$$NaO : CH : C \cdot C_6H_5 \cdot COOC_2H_5$$
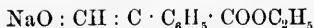
This gives immediately on acidification the liquid ester, and shows the intense coloration with ferric chloride. If, however, one allows a solution of the sodium compound in water to stand for even a minute before acidification, one obtains not the ϑ form, but crystals which are in every way characteristic of the β form, and which give no coloration with the ferric chloride solution.

This would show, that starting with the α ester one obtains a sodium derivative of that ester which, on solution in water, is so excessively unstable that inside of sixty seconds a tautomeric change takes place, converting the whole of the enol form to the keto form, which can therefore but have the constitution

$$HC{=}O$$
$$|$$
$$C_2H_5 \; C \; . \; Na \; . \; COOC_2H_5$$
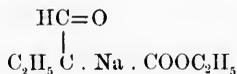
The remarkable behaviour of ethyl formyl phenyl acetate in alkaline solution towards acids under different conditions, and towards carbon dioxide must here be noticed, as it bears very directly on some of the results obtained in this paper.

If one dissolves indifferently either the α or β ester in dilute (normal) alkali, one obtains a solution which, according to the foregoing, must be regarded as the sodium derivative of the β form, because when an excess of acid is added there occurs an immediate precipitation of the aldo-ester.

If, however, the acid be added slowly and in small portions, one obtains at first the α ester, and finally a point is reached where the β ester is also thrown down. If carbon dioxide be led into the solution, one also gets as a first precipitation the oily ester and afterwards a crop of the crystals.

This would be explained by the assumption of a state of equilibrium, which in the first part of the reaction is disturbed by the precipitation of the less acid or α ester, which under slow acidification is again formed at the expense of the β compound. When, however, acidification takes place quickly, no time is given for the establishment of equilibrium, hence the oxymethylene derivative is precipitated at once.

The β sodium compound of ethyl formyl phenyl acetate reacts with copper sulphate or acetate, giving two derivatives which are fairly stable, and which correspond to the α and β modications. The latter is the less stable, and by allowing it to stand in the exsiccator, changes in the course of a few hours into the α modification. Here, also, without the use of a solvent one must assume a shifting of the copper atom from the formyl complex into the oxymethylene type.

From the behaviour of the sodium and copper derivatives of the formyl phenyl acetic ester in the solid state and in solution, one might naturally expect that by acting on these in a medium with small or large dissociation capacity, one would obtain with alkyl and acyl iodides compounds differing according to the position of the substituting groups.

As one may imagine in the case of a solution of a sodium compound in water, the sodium atom will be in great part dissociated, and there may be to a large extent a condition of partial freedom of the organic part of the molecule. In consequence of this, one has the substituting group entering at the position which from nature it has a tendency to select.

On the other hand, if one uses a medium like absolute ether, which allows of very little, if any dissociation, one will get direct substitution; i.e., a substitution occurring at the situation lately occupied by the metal. That this occurs will be shown in the case of formyl propionic ester.

Conversely it follows that by starting with a compound of definite configuration one can by no means be sure that the derivatives obtained by alkylizing or acylizing will have the same structural peculiarities which characterized the original substance.

Since writing the above, two papers have appeared by Robert Schiff on the "Tautomeric Forms of Aceto Acetic Ester and similar compounds." By taking different samples of acetoacetic ester, and condensing them with benzal aniline in the presence of traces of piperidine, or of sodium athelate, he has obtained benzal aniline addition products of aceto acetic ether, which belong to the enol form of that ether, and also to the ketol form. It would appear that the formation of oxymethylene compounds

by means of sodium ethylate, would in the highest degree tend to the formation of enol derivatives, and it is quite possible, could one perform this condensation with substances having a ketolizing action, that the tautomeric substituted acetic esters would be produced.

It would appear from Schiff's results that the influence of piperidine and sodium ethylate on the condensation of substituted acetic esters with benzal aniline is a general one, and it would be of interest to learn to what extent such syntheses can be accomplished in the oxymethylene series.

EXPERIMENTAL PART.

OXYMETHYLENE BENZYL CYANIDE.

Oxymethylene benzyl cyanide was prepared, according to Claisen's method, by condensing benzyl cyanide with amyl formic ester in absolute ethereal solution by means of metallic sodium in the form of wire. The sodium salt was decomposed by means of acetic acid, and the compound recrystallized from alcohol; it forms white needles, melting at 166°.

An attempt was made to prepare the sodium salt by acting on the cyanide with metallic sodium in absolute ether; no reaction took place, even after the mixture was allowed to stand some weeks. The compound was prepared by adding the calculated quantity of sodium ethoxide to a solution of the cyanide in absolute alcohol. The compound comes out as a white amorphous powder, of which more is obtained on adding absolute ether.

0·3282 gram of sodium salt gave 0·1392, Na_2So_4,
calculated for C_9H_6NONa 13·77%,
found,   13·74%.

Preparation of the Benzyl Compound.

In order to examine the behaviour of the sodium compound under different conditions of dissociation, it was benzoylated in aqueous solution and in ethereal suspension. For this purpose 5·5 grams of the dry salt were suspended in ether, and after being cooled with ice, 4·6 grams of benzoyl chloride were slowly added, the mixture being well stirred. No rise of temperature was observed. The mixture was allowed to stand over night in a cool place, and at the end of this time the sodium chloride and unchanged sodium compound filtered off and extracted ten times with ether. The ether evaporated and left a crystalline mass smelling strongly of benzoyl chloride. The residue was crystallized, first from ethyl acetate, and finally twice from dilute alcohol.

The melting point remained constant during alcohol crystallization: M.P. 117°–118°.

0·1600 gram of substance gave 0·4756 CO_2 and 0·0644 H_2O.

0·3222 "   "   "   15·4 ccs. moist nitrogen at 18°, and 741 mm. pressure.

$C_{16}H_{11}NO_2$ requires C=77·10°, H=4·41°, N=5·62°;

found   C=77·26°, H=4·44°, N=5·41°.

Action of Benzoyl Chloride on the Sodium Compound in aqueous solution.

5·5 grams of the sodium compound were dissolved in 50· ccs. of water in a stoppered flask, and the solution cooled externally by means of ice. 4·6 grams benzoyl chloride were then added gradually, the mixture being shaken constantly for two hours. At the end of this time the precipitate which had fallen had agglutinated to a soft mass. Dilute sodium hydrate solution was then added till the acid reaction had disappeared, and the soft mass further rubbed with the alkali till all smell of the acid chloride was no longer evident. The solid was then separated by means of the pump, well washed with water, and recrystallized from ethyl acetate and from dilute alcohol.

This presented the same characteristics as the compound obtained previously, coming down as short thick prisms, melting at 117°.

0·1988 gram substance gave 0·5642 gram CO_2 and 0·0794, H_2O.

0·2612 "   "   "   12·65 ccs. moist nitrogen at 17° and 735 mm.

Calculated for $C_{16}H_{11}NO_2$. C=77·10°, H=4·41°, N=5·44°;

found,   C=77·39°, H=4·43°, N=5·48°.

Hence oxymethylene benzyl cyanide gives but one acyl derivative on being benzoylated in absolute ether and in water.

Colorimetric Estimations.

0·2 gram of oxymethylene benzoyl cyanide was dissolved in 10 ccs. each of methyl alcohol, absolute ether and benzol. This was allowed to stand for 24 hours, and at the end of this time 2 ccs. of the solution taken and diluted to 10 ccs. with absolute alcohol and a single drop of ferric chloride solution added, and the coloured solutions examined in the Duboscq colorimeter. It will not be necessary here to give details of the colorimeter readings, which were carefully controlled by duplicate experiments. The results, however, would show that if one can take the lessening of colour as a criterion of the amount of ketolization occurring in dissociating media, the relation of the amount of aldo compound in alcohol to that in methyl alcohol was as 1 to 1·5321.

In the case of benzol and ether, the amount of ketolization was so small that no difference could be detected between the amounts obtained from the fresh solution of the oxymethylene ester and that to be found after the substance had stood in a solvent for 24 hours.

The Copper Salt of Oxymethylene Benzyl Cyanide.

1·45 gram of oxymethylene benzol cyanide was dissolved in 15 ccs. of alcohol, and 10 ccs. of a 10° solution of copper acetate added. There appeared to be a salt formed, so excessively soluble that it was immediately dissolved. Later on an amorphous dark green powder was precipitated ; this was separated and proved to be a basic salt of oxymethylene benzyl cyanide. It is insoluble in ether, alcohol and water, and gave on benzoylating the same benzoyl ether previously obtained.

OXYMETHYLENE CAMPHOR.

Oxymethylene camphor was prepared according to Claisen's direction, and further purified by distillation with steam. It forms a white crystalline mass, melting at 80°. The action of phenyl isocyanate on this compound has been previously investigated, and the coloration with ferric chloride was indicative of the enol form.

That the aldol compound of methylene camphor is not produced in a manner to be isolated is shown by the following experiments :

The sodium compound was dissolved in water, and the solution divided into two portions, one of which was made acid with dilute sulphuric acid, the other with carbon dioxide ; both operations were conducted in the cold. It appeared at first that the compound precipitated by means of the gas possessed a lower melting point than that obtained by sulphuric acid. This was found not to be the case on carefully repeating the experiment. The intensity of colour given by equal amounts of ferric chloride and of the respective compounds, was in all cases the same. Claisen's observation that the melting point of oxymethylene camphor is much depressed by traces of moisture, appears therefore to be correct.

The influence of carbon dioxide on the alkaline compound was next investigated :

The solution was made as cold as possible, and a slow stream of the gas led into the mixture. After a part of the oxymethylene camphor had been precipitated, the compound was filtered off quickly and carbon dioxide again passed in. Both these samples proved to be identical in melting point, ferric chloride reaction, etc.

A portion of the sodium compound was dissolved in iced distilled water, and ice cold dilute sulphuric acid added, and the mixture shaken out immediately with ether.

The ether solution was made up to 5 ccs., divided into two portions of 2½ ccs., and one portion evaporated on the water bath. After evaporation, both tests were made up to the same bulk, and a drop of ferric chloride solution added to each.

Absolutely no difference in the two tests could be observed.

This would show that even under the most favourable conditions aldolization in this compound does not take place.

That the aldol compound does exist in a state of equilibrium in solution together with the oxymethylene compound, is shown by the following colorimetric estimations :

Two grams of the oxymethylene camphor were dissolved in methyl alcohol, ether, and in benzol ; allowed to stand for 24 hours, and at the end of this time 2 ccs. of each were made up to 10 ccs., mixed with a single drop of ferric chloride solution, and compared in the colorimeter.

The intensity of colour was inversely to the dissociating capacity of the solvents. The colour produced by ether and benzol was practically alike ; that by ethyl alcohol was about half as strong, and methyl alcohol was again weaker.

ETHYL OXYMETHYLENE PROPIONATE.

Oxymethylene propionic ester was prepared according to the directions of W. Wislicenus, by condensing formic ethyl ester and propionic ethyl ester in absolute ether by means of metallic sodium.

The compound is volatile with ether vapour, and hence gives small yields, which can be increased by using a long Hempel's column or other similar device for distilling off the ether.

It boils at 142° at ordinary pressure. The sodium compound is easily prepared by treating the ester with sodium wire in absolute ether. It forms a yellowish white solid, which was dried in vacuo.

Preparation of Ester No. 1.

Instead of benzoylating this compound with benzoyl chloride, the p. nitro benzoyl chloride was used in order to get the melting point of the benzoate as high as possible.

1·85 gram of p. nitro benzoyl chloride was dissolved in 50 grams absolute ether, and after cooling with ice, 1·52 gram of the finely powdered sodium compound was added. The reaction takes place quickly, and at the end of 24 hours is at an end. The mixture was then filtered through a paper cone in a Soxhlet tube, and exhausted with ether. This left the sodium chloride in the cone, the ether dissolving out the benzoate. The benzoate was recrystallized three times from alcohol, and forms long slightly yellow needles, melting at 120°–121°.

0·1586 gram substance gave 0·3246 gram CO_2 and 0·0642 H_2O.

0·1332 gram substance gave 6·15 ccs. moist nitrogen at 19° and 647 mm.

Calculated for $C_{13} H_{13} NO_6$.

$$C = 55·91\%, \ H = 4·65\%. \ N = 5·01\%.$$
found, $$C = 56·11\%, \ H = 4·49\%, \ N = 5·22\%.$$

Preparation of Ester No. II.

1·52 gram of the sodium compound of oxymethylene propionic ethyl ester was dissolved in 50 ccs. of water, and after cooling 1·52 grams of p. nitro benzoyl chloride and a few drops of sodium hydrate solution added. The mixture was then shaken constantly for six hours. The ester which was precipitated was filtered off by means of the pump and recrystallized three times from alcohol. It had a melting point at least 20 degrees higher than the ester obtained from the ethereal solution. It melted constantly at 140°–142°, and gives the following results on analysis :

0·2142 gram gave 0·4408 gram CO_2 and 0 0822 gram H_2O.

0·3000 gram gave 14·0 ccs. moist nitrogen at 19° and 747 mm.

Calculated for $C_{13} H_{13} NO_6$.

$\quad$ C = 55·91%, H = 4·65%, N = 5·01%.

found, $\qquad$ C = 56·10%, H = 4·26%, N = 5·26%

It was now of importance to see which of the two compounds was the labile one, and if one were the more stable, to see if a shifting of the benzoyl group could be effected. In order to do this one gram of each was introduced into a small tube, the ends sealed, and both heated for an hour in the vapour of diphenylamine. B.P. 310°. Both charred, and on extracting the charred residues with alcohol no crystalline products were obtained.

The substances were next distilled in vacuum, and in which they boil without decomposition. Benzoate No. 1 boils at about 215°–217° at 15 mm., but did not appear to be changed, as the melting point remained the same as before (120°).

The desired effect was produced by heating the two substances in closed tubes in a bath of sulphuric acid at 245°–250° for five minutes. After recrystallization both melted sharply at 140°.

If one assumes that the two isomers are not stereoisomeric in the sense of fumaric and maleic acids, and are not to be represented by the formulæ

$$HC \cdot OOC \cdot C_6H_4NO_2 \qquad\qquad C_6H_4NO_2C \cdot OO \cdot CH$$
$$\|\qquad\qquad\qquad\qquad\qquad\qquad \|$$
$$CH_3C \cdot COOC_2H_5 \qquad\qquad\quad CH_3C \cdot COOC_2H_5$$
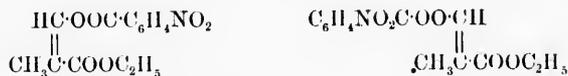
but by the tautomeric formulæ

$$H \cdot C \cdot OOC \cdot C_6H_4NO_2 \qquad\qquad\qquad H \cdot C : O$$
$$\|\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$CH_3C \cdot COOC_2H_5 \qquad\qquad\qquad CH_3C \cdot COOC_2H_5$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad OC \cdot C_6H_4NO_2$$

it follows that the change of one of these substances into the other must be the result of the shifting of the heavy benzoyl group from one part of the molecule to the other in an analogous manner to Claisen's example of isopropenyl ethyl ester.

One cannot, of course, fix either of the tautomeric configurations to the formula of one or of the other of these compounds, but it is safe to conclude that the isomerism is tautomeric and not stereoisomeric.

Oxymethylene propionic ester was examined with Professor Drude's apparatus for anomalous absorption, and the results obtained by this method prove conclusively that the ester had the enol configuration, as the absorption for electric oscillations was of the most marked type.

Oxymethylene Succinic Ester.

Oxymethylene succinic ester was prepared according to the direction of Wislicenus, by treating ethyl succinate with ethyl formate in the presence of sodium in absolute ethereal solution.

The reaction does not proceed smoothly, and must be carefully watched, for if the mixture be made too cold the reaction does not take place readily, and, on the other hand, if the temperature rise, the mixture boils, and large quantities of succinylosuccinic ester are formed.

Oxymethylene succinic ester is an oil boiling at 135° at a pressure of 20 mm.

The action of p. nitro benzoyl chloride on oxymethylene succinic ester.

If the sodium compound of oxymethylene succinic ester be benzoylated according to the ordinary Schotten-Baumann method, the yield is by no means good, so that one proceeds in the following way:

The ester is dissolved in the calculated quantity of normal sodium hydrate in a small stoppered flask, and covered with a layer of ether. One molecule of p nitro benzoyl chloride is then added, also a few drops of sodium hydrate solution, the flask is then continuously shaken for an hour, at the end of which time the bottle is filled with a mass of silky needles. These are filtered off and recrystallized from dilute alcohol. The compound melts sharply at 104°. It gave the following numbers of analysis:

0·2260 gram gave 0·4526 gram CO_2 and 0·0982 gram H_2O.

0·2742 gram gave 10·4 ccs. moist nitrogen at 22° and 751 mm.

$C_{16} H_{17} NO_8$ requires C = 54·70%, H = 4·82%, N = 3·98%.

found,   C = 54·61%, H = 4·82%, N = 4·13%.

The oxymethylene succinic ester was also benzoylated in ethereal solution. For this purpose 2·02 grams of the ester were dissolved in absolute ether, and to this 0·23 gram of sodium wire added. After the ester had been completely converted into the sodium derivative, the cal-

culated quantity of p. nitrol benzoyl chloride was added, and the mixture allowed to stand for some days.   After filtering from the sodium chloride the ethereal solution was evaporated, and the residue crystallized from alcohol several times.

The melting point of the compound was identical with that of the preceding, namely, 104°.

It gave the following numbers on analysis :

$C_{16} H_{17} NO_8$ requires C = 54·70%, H = 4·82%.
found,   C = 54·99%, H = 4·89%.

The Preparation of the Copper Compound.

4·04 grms of oxymethylene succinic ester were dissolved in a little alcohol, and 1·99 gram of cupric acetate in a 10% solution in water added.   On strongly cooling the mixture the copper compound is precipitated in splendid long green silky needles, which on crystallization from alcohol melt at 133°–135°.

0·3261 gram gave, on ignition. 0·0545 gram Cu O.

Calculated for $C_{18} H_{26} O_{10}$ Cu.

Cu = 13·54%.

found,   13·25%.

The colorimetric estimations of oxymethylene succinic ester were carried on in exactly the same way as with the previous compounds. The difference in colour after the solutions were allowed to stand was so marked that no comparison could be made.   In the case of oxymethylene alcohol, the ketolization appeared to have gone so far that with ferric chloride scarcely any colour could be observed.

Oxymethylene succinic ester shows marked absorption for electric oscillations when examined with Drude's apparatus.   This result was in accordance with the chemical results obtained above.

### The Relation of Oxymethylene Succinic Ester to Aconic Acid.

Oxymethylene succinic ester bears a close relation to aconic acid, which has been investigated by Kekulé, Beers, Swarts and Meilly.

Reitter, in an investigation of the methyl ester of aconic acid, has shown that this ester reacts with phenyl hydrazine, giving two compounds melting at 167° and 178° respectively.

The formula which he ascribes to the first is that of a hydrazone-hydrazide of the hypothetical oxyaconic acid ; to the second, a hydrazone-dihyrazide of the same compound.

The following experiments would tend to show that in the action of phenyl hydrazine on oxymethylene succinic ester, two substances are

formed. One has a melting point of 110°, and gives analytical results agreeing with the pyrazolone formula

$$N \cdot C_6H_5$$

$$\begin{array}{cc} OC & N \\ | & \| \\ COOC_2H_5 \cdot CH_2HC\!\!-\!\!-\!\!CH \end{array}$$
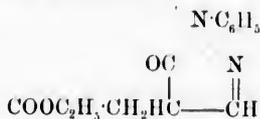
Oxymethylene succinic ester on treatment with excess of phenyl hydrazine, or treating the pyrazolone with another molecule of the same reagent, a splitting of the pyrazolone ring takes place with the formation of the hydrazone-dihydrazide of formyl succinic acid.

The compound melting at 167° was not obtained.

It is now of interest, considering that oxymethylene succinic ester is the ester corresponding to the lactonic aconic acid, to investigate the action of phenyl hydrazine on this former substance, for in this way it was that some light might be thrown upon the constitution of aconic acid, which has been variously represented by the following constitutions:

$$\begin{array}{cc} COOH & COOH \\ HC = C - CH_2 & H_2C - C = CH \\ | \quad | & | \quad | \\ O - CO & O - CO \end{array}$$

4 grams of formyl succinic ester were mixed with two grams of phenyl hydrazine freshly distilled. The mixture immediately became hot and turned deep red. It did not solidify in a freezing mixture. It was then heated for some hours on the water bath, and finally in a paraffin bath at 160°. On cooling and adding a very little ether, the mass set perfectly solid. The substance was recrystallized from low boiling petrolic ether, and then from alcohol by dissolving at 70° and placing the solution in the freezing mixture. The substance melted at 110°. It gave the following numbers on analysis:

0·1273 gram gave 0·2961 gram CO_2 and 0·0654 gram H_2O.

0·1676 gram gave 17·1 ccs. moist nitrogen at 23° and 750 mm.

Calculated for $C_{13}H_{14}N_2O_3$.

$$C = 63·41\%, \; H = 5·69\%, \; N = 11·34\%.$$

found, $\quad C = 63·41\%, \; H = 5·70\%, \; N = 11·39\%.$

It is, therefore, the pyrazolone ester of 1 phenyl pyrazolone, 4 acetic acid.

An attempt was made to obtain the acid corresponding to the pyrazolone ester by hydrolyzing the ester, but no definite compound could be isolated.

In order to ascertain whether by the treatment of the pyrazolone ester with excess of phenyl hydrazine a splitting of the ring could be

effected with the formation of the hydrazone-hydrazide, a quantity of the pyrazolone, melting at 110°, was treated with phenyl hydrazine at 160° in a paraffin bath. On crystallizing, a compound was obtained, the melting point of which was found to be 190°, and gave the following numbers on analysis:

0·2268 gram gave 0·5490 gram CO_2, and 0·1088 gram H_2O.

0·0697 gram gave 12·8 ccs. moist nitrogen at 23° and 746 mm.

Calculated for $C_{23} H_{24} N_6 O_2$.

$$C = 66·34\%, H = 5·75\%, N = 20·19\%.$$

found, $C = 66·01\%, H = 5·32\%, N = 20·46\%.$

The same compound was prepared by treating oxymethylene succinic ester with two molecules of phenyl hydrazine, which gave the same compound melting sharply at 190°, and a nitrogen determination gave a nitrogen content of 20·55%.

It is therefore evident that the pyrazolone obtained by the treatment of oxymethylene succinic ester with one molecule of phenyl hydrazine, on the addition of another molecule of the reagent, splits according to the following:
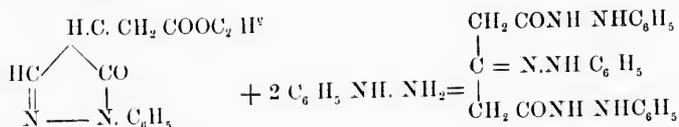
giving the hydrazone-hydrazide of formyl succinic ester.

Experiments with Formyl Phenyl Acetic Ester.

As formyl phenyl acetic ester shows such a marked tendency towards ketolization in dissociating media, it is of interest now to ascertain what effect substituted hydrazines would have on solutions of the ester which had been allowed to stand for some time. For this purpose a quantity of formyl phenyl acetic ester was heated at 70° for some hours in order to convert it completely into the enol form and one gram of the ester was dissolved in 50 ccs. respectively of methyl alcohol and of benzol. After 24 hours standing the calculated quantity of phenyl hydrazine freshly distilled was added and the mixture allowed to stand 48 hours. On the addition of the reagent, the methyl alcohol solution became slightly coloured, the benzol solution inside of ten minutes was a deep yellow, and on standing 24 hours the colour of the methyl alcohol solution was deep yellow, while that of the benzol was deep green. There appeared to be in the benzol drops of water deposited.

The solvents in both cases were distilled off at the room temperature, by placing the receivers connected with the flasks containing them in a freezing mixture, and evacuating. The methyl alcohol solution left a

pale yellow mass which became fluid at the temperature of the room, and set in the freezing mixture.

The benzol solution gave a semi-crystalline green mass which remained solid at the room temperature. The benzol solution when allowed to stand for some time deposited crystals which, when filtered off and dried on a porous tile, melted at 192°.

Both the residues above mentioned on being exposed to air for 48 hours turned red. It appeared to be impossible to isolate from either of these residues a definite crystalline product, although the benzol residue was to a large extent crystalline.

The behaviour of the residues dissolved in concentrated sulphuric acid was quite similar. They dissolved with a deep red colour. A crystal of potassium bichromate makes the colour markedly deeper.

The methyl alcohol residue was heated in a test tube over a free flame. A lively reaction ensued and alcohol was given off. The oil set to a crystalline mass. This was dissolved in alcohol and water added, and comes down again as a light brown substance identified with the 1·4. methyl phenyl pyrazolone melting at 192°, not sharp. It was also identified by the pyrazolone reaction with sulphuric acid and ferric chloride.

The benzol residue gave a similar yield of the same compound.

The Action of p. Bromphenyl Hydrazine.

2 grams of formyl phenyl acetic ester were dissolved in 100 ccs. of methyl alcohol and 100 ccs. of benzol respectively, and allowed to stand 24 hours. After this time the calculated quantity of the hydrazine was added and the mixture allowed to stand at ordinary temperature. After a lapse of 12 hours the benzol solution had become turbid, and after 24 hours had deposited a somewhat large quantity of crystals. These were filtered off and the solution evaporated in vacuo at the ordinary temperature.

The crystals so obtained after crystallization from alcohol in which they are sparingly soluble, melted with decomposition at 255° and gave the pyrazolone reaction.

The solution on evaporation gave a semi-solid mass, which was placed on porous plates and washed with a little alcohol and recrystallized from alcohol, in which it is quite soluble when hot and only slightly so when cold. It has also a melting point of 255°. It gave the following numbers on analysis :

0·1030 gram gave 0·0614 gram AgBr.

Calculated for, $C_{15} H_{11} N_2 BrOBr = 25·41\%$.

found, $Br = 25·36\%$.

The methyl alcohol solution on being treated in the same way gave a yellow paste which did not solidify but stiffened in the freezing mixture.

On heating to 100° on the water bath, it gave a dry yellow cake which was soluble with difficulty in alcohol and was recrystallized from it. It also melted at 255°. It gave the following numbers on analysis :

0·1915 gram gave 0·1106 gram AgBr.

Calculated for $C_{15}H_{11}N_2$ BrOBr $= 25·41\%$.

found,   Br $= 24·52\%$.

It is hence the 1·4. phenyl p. bromphenyl pyrazolone.

CONCLUSIONS.

1. The substances investigated in this paper were oxymethylene benzyl cyanide, oxymethylene camphor, oxymethylene propionic ester and oxymethylene succinic ester. It has been demonstrated that, although tautomeric change can be detected in solution, in some cases the change being of apparently large dimensions, the compounds are only capable of existing in the enol modification.

2. Oxymethylene propionic ester is the only one of these compounds which gives isomeric acyl derivatives, the lower melting one is capable on heating at a high temperature of transformation into the higher melting modification.

3. Oxymethylene phenyl acetic ester does not give isomeric compounds on being treated with phenyl hydrazine in media of different dissociating capacities.

4. One of the products formed by the treatment of formyl succinic ester with phenyl hydrazine, is identical with that obtained by Reitter from methyl aconate.

I wish here to thank Professor W. Wislicenus for his kindness in allowing the experimental part of this work to be presented to this society, and also for the help which he extended me during the course of this work.

I intend to study the therapeutic action of the tautomeric compounds which have been presented in this paper, and experiments have already been commenced in this direction.

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