XX.—*On the Constitution of Dehydracetic Acid.*

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DURING an investigation of the action of heat on ethylic β -amido-crotonate (on which I have been engaged for some years) I was much struck with the partial decomposition this ethereal salt undergoes when distilled, yielding ethylic lutidonecarboxylate, a pyridine derivative.

This decomposition forcibly recalls the formation of dehydracetic acid from ethylic acetoacetate when the latter is heated, and the fact that dehydracetic acid itself gives lutidone when treated with ammonia still further increases the resemblance. I was naturally led, therefore, to inquire into the formulæ which various investigators have proposed for dehydracetic acid. This peculiar compound has for long been the subject of investigation, but the various formulæ which have been suggested are all open to criticism, as Feist, in his excellent paper on this acid (*Annalen*, **257**, 253), has shown; and as he discusses this question in detail, it is needless to again go over the ground. I shall, therefore, only take the formula given by Feist,

and show where I think it is inadequate to explain all the known properties and reactions of dehydracetic acid.

Dehydracetic acid is formed by the action of heat on ethylic acetoacetate, alcohol, water, and ethylene being produced at the same time, the best process for its manufacture being to allow a slow stream of ethylic acetoacetate to run into an iron tube filled with pumice stone and heated in a combustion furnace. In this way, nearly the whole of the ether is converted into dehydracetic acid.

That dehydracetic acid is a true acid, containing the carboxyl group, was for some time thought to be the case. Ostwald, however, contradicts this,* showing that, from measurement of the conductivity of the acid, the dissociation constant obtained is about 200 times too small, as compared with the constant of such acids as salicylic acid. It therefore probably resembles the phenols or else compounds such as ethylic acetoacetate or ethylic malonate.

Dehydracetic acid does not give an acetyl derivative, but when treated with phenylhydrazine, or hydroxylamine, the ordinary reaction occurs which takes place when a carboxyl group is present.

With pentachloride of phosphorus, it gives a dichloride, two hydroxyl groups being replaced by chlorine; this reaction at first sight seems to contradict the non-formation of an acetyl derivative, but in all probability it can be explained by the peculiar nature of the acid, as it contains the residues of two ethylic acetoacetate molecules, and it is quite conceivable that, as in the case of ethylic acetoacetate, the following reaction takes place:—

and then hydrochloric acid splitting away the group

would remain.

On warming with alkalis, a complete decomposition of the molecule takes place, and the same products are obtained as when ethylic acetoacetate is treated in a similar manner.

Dehydracetic acid yields pyridine derivatives with great ease when heated with ammonia, but this is probably due to a partial rearrangement of the molecule after the addition of the elements of water and the subsequent elimination of carbon dioxide.

Most of the methods of formation and also of the decompositions of the dehydracetic acid are well explained by Feist's formula; for instance, the decomposition, when boiled with alkalis, which yields a carbonate and acetate of the alkali and acetone,

* Ostwald, "Über die Affinitätsgrößen organischen Säuren und ihrer Beziehung zur Zusammensetzung und constitution derselben." Leipzig, 1889.

and by an ingenious reaction, the formation of the pyridine derivative, lutidone, where the two methyl groups are in the $\alpha\alpha'$ -position, is also accounted for.

When we come to the production of a dichloride, where apparently two hydroxyl groups are replaced by chlorine, we at once perceive the inadequacy of the "*wahre Constitutions-formel*." The production of orcinol and the formation of a methylic ether possessing acid properties are also not easy of explanation. The expression made use of by Feist "*wahre Constitutions-formel*" may be regarded in the light of a challenge to other chemists to devise a formula better adapted to express all the changes which take place during the formation and decompositions of dehydracetic acid; and the considerations which

follow *per se*. I venture to think that the last has not been said on the subject.

There are two formulæ which might possibly be preferable to Feist's. The first, in which the two methyl groups are in the $\alpha\alpha'$ -position, thus—

and where, instead of alcohol being eliminated in the ϵ -lactone position, the β -position is used. The production of lutidone would by this formula be as follows:—

It is probable, however, that if this were the case, the formula for dehydracetic acid would be $\text{C}_{16}\text{H}_{16}\text{O}_8$, as it would belong to the class of lactides. This is not so, as a determination of its molecular weight by Raoult's method gave the following result:—

0.600 gram substance lowered the m. p. of 35.05 grams acetic acid
0.40° C.

	Found.	Calculated for $\text{C}_8\text{H}_8\text{O}_4$.
Mol. weight.....	167	168

But the formula which I next propose still more satisfactorily explains the reactions of dehydracetic acid, and not only accounts for these reactions of dehydracetic acid where Feist's formula fails, but also throws additional light on the formation and constitution of many other substances as well as dehydracetic acid.

It is well known that the acetyl group easily reacts in the following way:—

as in the formation of mesityl oxide and mesitylene,

cinnamic acid from benzaldehyde and acetic acid, and in many other cases when the methyl group is attached to an electro-negative group. If we apply this to acetoacetic ether, we get the following reaction :—

But alcohol and ethylene are also produced during the preparation of dehydracetic acid,

and the substance remaining is therefore a δ -lactone, which can be written—

We see now that dehydracetic acid contains two hydroxyl groups; hence it will react with pentachloride of phosphorus, giving

The replacement of the hydrogen of one hydroxyl group by methyl still leaves another hydroxyl group which can react with sodium, yielding a sodium compound; and if the acid property of dehydracetic acid is due to the presence of these groups, the monomethyl ether would probably possess acid properties. This, however, is not to be insisted on, as the acid reaction of dehydracetic acid may quite possibly be due to the presence of the methylene groups which are placed between the carbonyl groups.

The formation of orcinol by heating the acid with baryta-water also follows easily :—

The production of dehydracetic acid from chloride of acetyl by heating it with pyridine is also easy to understand:—

The formation of lutidone is also accounted for by the elimination of water from the δ -lactone position—

with ammonia and water gives—

Dehydracetic acid, when boiled with alkalis, yields acetic acid, acetone, and carbonic acid:—

Malonic acid is also sometimes produced:—

The bromine derivative would have the following formula:—

and the compounds produced by the action of nascent hydrogen are—

Feist, by heating dehydracetic acid with hydriodic acid in a sealed tube, converted it into the $\alpha\alpha'$ -dimethylpyrone,

This substance he also produced by heating an acid that he obtained by the action of sulphuric acid on the dichloride. This acid is isomeric with dehydracetic acid. The measurements of its conductivity by Oswald show that it evidently contains a carboxyl group, and Feist calls it the "*wahre Dimethylpyrone-carbonsaure*," and gives it the following constitution:—

This is the formula originally suggested for dehydracetic acid by Perkin.

If, however, the formula for the dichloride be

then, by elimination of hydrogen chloride and the addition of the elements of water, we get—

or

and Feist's dimethylpyronecarboxylic acid becomes—

which on heating would lose carbon dioxide and give $\alpha\alpha'$ -dimethylpyrone; the true dimethylcarboxylic acid has therefore yet to be produced.

If therefore the formula which I have given to dehydracetic acid be the correct one, it is not a derivative of pyrone,

as Perkin suggested in his paper (Trans., 1887, 489), but of oxypyrone, or the δ -lactone of β -oxycacrylylacetic acid,

The compounds meconic acid, comenic acid, and pyromeconic acid, which seem to be connected with pyrone or oxypyron, might possibly have the following formulæ, thus—

Comenic acid, which is formed by the elimination of carbon dioxide from meconic acid by heat, would be—

and pyromeconic could only be—

or the δ -lactone of β -oxyacrylylacetic acid.

Coumalinic acid, as Pechmann and Welsh have shown (*Trans.*, 1885, **47**, 149), also probably belongs to this δ -lactone class—

The decomposition which these meconic acid compounds undergo when boiled with alkalis, acetone being formed, can now be easily understood.

Closely connected with these oxypyrrone compounds are the true pyrrone compounds, to which class chelidonic acid no doubt belongs—

There probably also exists an analogous series of compounds, containing a carbonyl group fewer than pyrrone and oxypyrrone derivatives; this series is the furfuran and oxyfurfuran class:—

and as ammonia gives pyridine derivatives with the one class, so it should yield pyrrolene derivatives with the other. Several instances might be given of the furfuran compounds, thus—

and to the oxyfurfuran class belong aconic acid and the ketolactonic acid of Young (*Annalen*, **216**, 45),

The production of the ketolactonic acid is of some interest, as it is formed in small quantities during the distillation of ethylic β -ethyl-acetosuccinate, in the same manner as dehydracetic acid is produced from ethylic acetoacetate—

or

It is hardly necessary to point out the fact that if the above be the correct explanation of the production of dehydracetic acid from ethylic acetoacetate, then dehydrobenzoylacetic acid must be formed by another reaction, as it does not contain a methyl group. That this is so is rendered possible by the reactions of dehydrobenzoylacetic acid, notably the action of pentachloride of phosphorus; and the formula suggested by Feist (*Ber.*, **18**, 3725) may be the correct one.

Closely connected with dehydracetic acid is the dihydrodiacetyl-lævulinic acid of Magnanini (*Gazzetta*, **19**, 275); it is, in all probability, the next higher homologue of the dehydracetic acid series—

$\text{C}_4\text{H}_6\text{O}_3$
Acetoacetic acid.

$\text{C}_6\text{H}_8\text{O}_4$
Dehydracetic acid.

$\text{C}_7\text{H}_9\text{NO}$
Lutidone.

$\text{C}_5\text{H}_8\text{O}_3$
Lævulinic acid.

$\text{C}_9\text{H}_{10}\text{O}_4$
Dihydrodiacetyl-
lævulinic acid.

$\text{C}_8\text{H}_{11}\text{NO}$
 α -Methyl- α -acetyl-
pyrrolene.

It was obtained by heating lævulinic acid to a very high temperature with acetic anhydride. It easily yields, with ammonia, a compound which has the formula $\text{C}_8\text{H}_{11}\text{NO}$, which in its turn gives, when heated with zinc-dust, pyrrolene, and not *pyridine*.

The δ -lactone formula for dehydracetic acid shows at once how this is possible—

In this case, by the action of ammonia on the acid, together with water, there is no *hydroxyl group in the δ -position to the nitrogen atom*;

consequently a γ -imido- or pyrrolene compound is formed. If then dehydracetic acid is the δ -lactone of the formula—

it is probably formed by the condensation of 4 mols. of acetic acid, as Geuther first suggested in 1866, when he gave it the name dehydracetic acid—

or

then

and it is the δ -lactone of *tetracetic acid*; and the following list shows the connection between the condensed acids of acetic acid—

But the tri- and tetra-acids would of course yield at once δ -lactones.

Up to the present time, triacetic acid does not seem to have been obtained, unless the carbacetic acid of Duisberg, $\text{C}_6\text{H}_8\text{O}_3$, be identical with its lactone. The ethyl ether of this acid was obtained by allowing a solution of hydrogen chloride in ethylic acetoacetate to stand for four weeks.