compound with 25.0 cc. of 0.5 N mercuric chloride. The precipitate settles rapidly, and there is no difficulty in making comparison tests.

To adapt the method for class use, the following directions were formulated:

"Dissolve the residue of mercury and amido mercuric chloride (Group I)[1] or the residue of mercuric sulfide, and double sulfide and nitrate ($Hg_3S_2(NO_3)_2$) (Group II)[1] in *aqua regia*, and evaporate nearly to dryness, *i. e.*, till only 0.5 to 1.0 cc. of liquid is left. Add 10 cc. water and filter. Wash the residue, if any, with two portions of water, each 2.5 cc. in volume, adding to the filtrate. Now add to this filtrate 10 cc. three-normal sodium hydroxide, and then 25 cc. of the following mixture: 10 cc. three-normal sodium hydroxide, 10 cc. three-normal ammonium hydroxide and 5 cc. half-normal potassium iodide. Red or brown-red precipitate indicates mercury. Make comparison tests by adding 25 cc. of the above test reagent to 25 cc. of a mercuric chloride solution of known concentration since a 25 cc. portion of the unknown was used for analysis."

In the hands of students having had absolutely no experience in the detection of mercury, this method has yielded excellent results where ordinary care and intelligence has been exercised. The main points to note are that the excess of *aqua regia* must be removed and that the mercuric chloride must not be volatilized by overheating the solid residue left on evaporation. In laboratories where concentrations are not reported by the students, the alkaline ammoniacal iodide solution should be added drop by drop, taking care, however, that the solution to be tested is neutral or alkaline before making the test.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONSTITUTION OF DEHYDROACETIC ACID.

BY WILLIAM J HALE.

Received April 22, 1911.

The construction of a satisfactory structural formula for dehydroacetic acid has occupied the attention of chemists ever since its discovery by Geuther[2] in 1866. He obtained this crystalline substance from the decomposition products of acetoacetic ester, but attempted nothing beyond its empirical formula, $C_8H_8O_4$. The determination of its correct structure has become highly important by reason of the great variety of well-known and important compounds that can readily be prepared from it, such, for

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[1] See Böttger's "Qualitative Analysis," Smeaton's translation, 1906 ed., pp. 9 and 24 for analysis on this point.

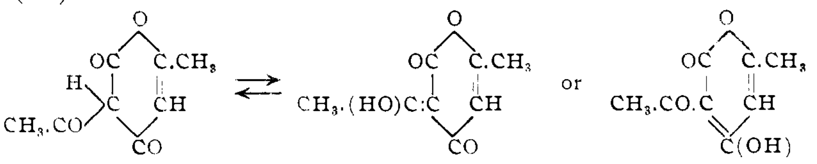
[2] *Jena'sche Zeitschrift*, II, 387 (1866).

example, as diacetyl acetone, lutidone, dimethylpyrone, and others. No doubt much of the difficulty that confronted the correct interpretation of observations with this acid lay in the possible existence of two ionizable hydrogen atoms. Ordinarily there is but one acid hydrogen, a hydrogen linked to a carbon atom which is adjacent to three carbonyl groups, yet when this hydrogen is replaced by a methyl group a second acid hydrogen makes its appearance.

The formula proposed by Oppenheim and Precht,[1] as well as that by Haitinger[2] and also by W. H. Perkin, Jr.,[3] accounted for this acidity, through the presence of a carboxyl group. Ostwald[4] showed that this assumption was entirely unfounded by reason of the small dissociation constant (K = 0.00053) and proposed for the acid a formula according with monoacetyltriketohexamethylene, an hypothesis, however, which could not be substantiated by experimental evidence.

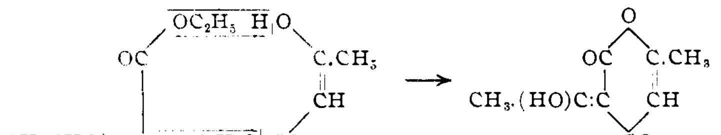
Schibbye[5] even supposed this acid to have a structure in the form of an eight-membered ring.

In 1890 Franz Feist[6] proposed his "wahre Constitutionsformel" for dehydroacetic acid. In this we have a derivative of pyronone (a keto-dihydropyrone) of the constitution (I), or a 6-methyl-3-acetopyronone; a compound which may also present two possible tautomeric forms (II) and (III):



I. II. III.

The acid is, therefore, to be considered as a δ-lactone and produced (in tautomeric form) from two molecules of acetoacetic ester in the following manner:



In 1891 J. Norman Collie[7] proposed a formula (IV) for dehydroacetic

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[1] *Ber.*, 9, 323 (1876).

[2] *Monatsh.*, 6, 103 (1885); *Ber.*, 18, 452 (1885).

[3] *J. Chem. Soc.*, 51, 484 (1887).

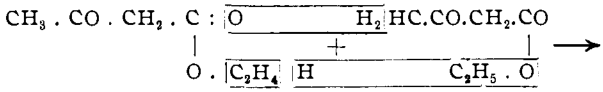
[4] "Ueber die Affinitätsgrössen organischer Säuren und ihre Beziehungen zur Zusammensetzung und Constitution derselben," W. Ostwald, Leipzig, 1889.

[5] Inaugural Dissertation, Würzburg, 1882.

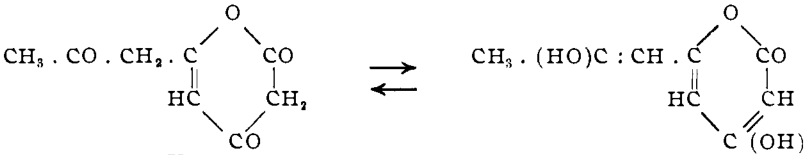
[6] *Ann.*, 257, 253 (1890).

[7] *J. Chem. Soc.*, 59, 179, 617 (1891).

acid somewhat different from that of Feist's. An acetonyl group is here considered as a side-chain in the α-oxypyrone (or pyronone) ring. This constitutes a 6-acetonylpyronone and differs from Feist's formula only in respect to the acetyl group, which now is considered as replacing a hydrogen atom of the methyl group in the 6-position as shown by Feist. The basis for this formula rests upon well substantiated evidence for the possible condensation of the oxygen of an acetyl group with two hydrogen atoms of a methyl group adjacent to a carbonyl. The application to acetoacetic ester may be looked upon (according to Collie) as proceeding in the following manner:



$$\begin{array}{l} CH_3 . CO . CH_2 . C : \boxed{O \qquad H_2} HC.CO.CH_2.CO \\ \qquad\qquad\qquad\quad | \qquad\qquad + \qquad\qquad\qquad | \quad \longrightarrow \\ \qquad\qquad\qquad\quad O . \boxed{C_2H_4} \; \boxed{H \qquad C_2H_5 . O} \end{array}$$



IV. V.

The presence of ethylene is usually detected in the decomposition of acetoacetic ester, hence its occurrence was thought to be accounted for most simply by the reaction just given. Feist[1] later pointed out the important fact that when also a methylene group is present and adjacent to a carbonyl group there is not so marked a tendency for the methyl group to enter into condensation.

The Collie formula adequately explained all of the reactions in which dehydroacetic acid had so far been concerned. It satisfactorily accounts, in its tautomeric form (V), for the formation of a dichloride (by action of phosphorus pentachloride), where apparently two hydroxyl groups are replaced by chlorine. The slight acidity noted in the monomethyl ether of dehydroacetic acid may likewise be attributed to the possible existence of the second hydroxyl. The Feist formula can only account for one possible chloride by replacement of an hydroxyl group. This failure to explain the formation of a dichloride has indeed been one of the strongest arguments against the Feist formula. Feist,[2] however, has stated that the formation of the dichloride is by no means a simple process, but presumably one in which the ring itself is opened, as is the case when ammonia and amino-derivatives react upon this acid.

The production of dehydrobenzoylacetic acid,[3] by prolonged heating of benzoyl acetic ester, can not (as Collie admitted) be expected to result

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[1] *Ber.*, **25**, 342 (1892).

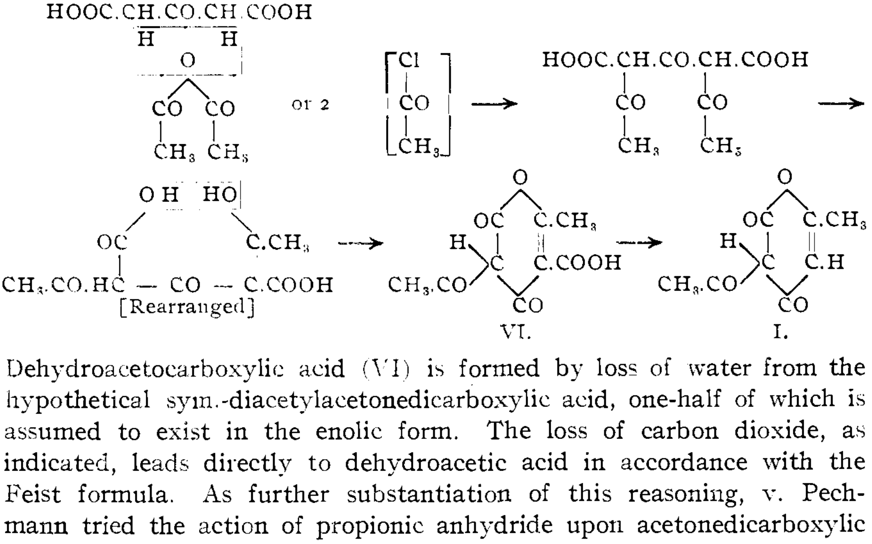
[2] *Ibid.*, **25**, 432 (1892).

[3] *J. Chem. Soc.*, **47**, 277 (1885).

from this manner of condensation. Though the structure of dehydroacetic and dehydrobenzoylacetic acid[1] are no doubt identical, the latter must arise from some other reaction. Collie's formula may be considered as the δ-lactone of hydroxyacrylylacetic acid; or again, and more pointedly emphasized by Collie, the δ-lactone of tetracetic acid. This hypothetical tetracetic acid may be looked upon as the result of condensation between four molecules of acetic acid, $CH_3.CO.CH_2.CO.CH_2.CO.CH_2.COOH$, a supposition quite in keeping with Geuther's first hypothesis of the dehydration of acetic acid alone, hence the name as then proposed.

v. Pechmann,[2] in his studies upon acetonedicarboxylic acid, announced a new method for the preparation of dehydroacetic acid. This method consisted in warming gently a mixture of acetonedicarboxylic acid and acetic anhydride; the product formed is a dehydroacetocarboxylic acid, which when sublimed readily loses carbon dioxide to give dehydroacetic acid itself. v. Pechmann found also that acetyl chloride reacted equally as well upon acetonedicarboxylic acid and yielded the products just mentioned. The classical investigations by v. Pechmann in this field pointed more particularly to the Feist formula for dehydroacetic acid.

In support of Feist's formula v. Pechmann outlined the following series of reactions:



VI. I.

Dehydroacetocarboxylic acid (VI) is formed by loss of water from the hypothetical sym.-diacetylacetonedicarboxylic acid, one-half of which is assumed to exist in the enolic form. The loss of carbon dioxide, as indicated, leads directly to dehydroacetic acid in accordance with the Feist formula. As further substantiation of this reasoning, v. Pechmann tried the action of propionic anhydride upon acetonedicarboxylic acid. The result was a dehydropropionylacetocarboxylic acid (VII) which, by loss of carbon dioxide, readily gave the expected dehydropropionylacetic acid (VIII). By analogy, formula (IX) would represent the structure of dehydrobenzoylacetic acid.

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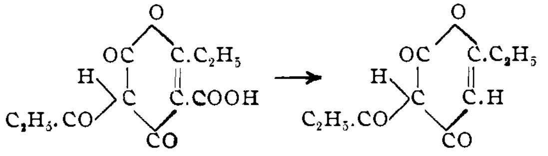
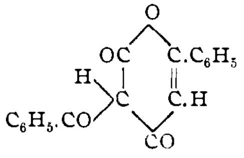
[1] Baeyer and Perkin, *Ber.*, 17, 64 (1884); *Ibid.*, 18, 3726 (1885).

[2] *Ber.*, 24, 3600, 4098 (1891); *Ann.*, 273, 186 (1893).

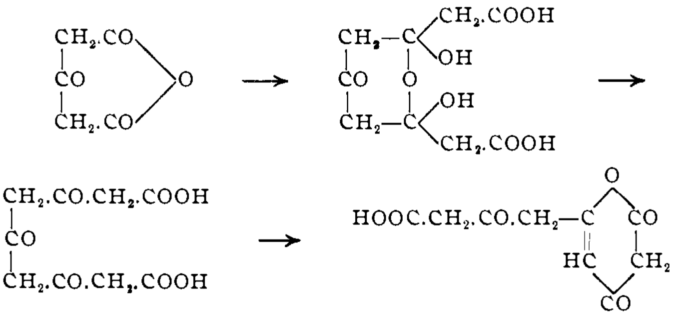


VII. VIII.



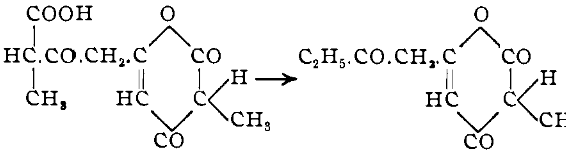
IX.

If the Collie formula is the correct one then an entirely different mode of condensation must here be considered.[1] Acetonedicarboxylic anhydride is first formed; this in turn reacts with one molecule of acetic anhydride to form a dicarboxylic acid which, upon heating, adds water to open the ring and then passes over into a diacetylacetonedicarboxylic acid; this latter forms at once the lactone or dehydroacetocarboxylic acid (X) and finally by loss of carbon dioxide yields dehydroacetic acid itself (IV):

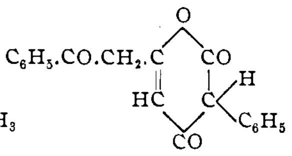


X.

According to Collie, therefore, the constitution of v. Pechmann's dehydropropionylacetocarboxylic acid must have a similar constitution (XI) to give eventually dehydropropionylacetic acid (XII). And dehydrobenzoylacetic acid, whether or not formed in this manner, should have, according to Collie, the structure (XIII):



XI. XII.



XIII.

Since the extensive work of Feist and Collie on this acid, a number of others have contributed much toward its final solution. Dieckmann and Breest[2] showed that the action of acetylchloride upon triacetic lactone need not be construed as an argument against Feist's formula as Collie

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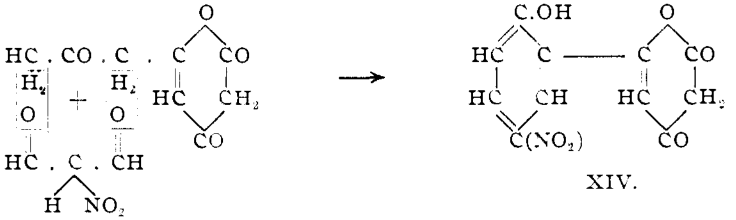
[1] *J. Chem. Soc.*, 77, 977 (1900).

[2] *Ber.*, 37, 3387 (1904).

has suggested.[1] Stollé[2] in studying the action of phenylhydrazine upon dehydroacetic acid came to the conclusion that a true phenylhydrazone is here formed. This compound, by the action of acid, yielded a condensation product which could not be accounted for upon the Collie formula. Bülow[3] sought to show a different mode of condensation of this acid with N-amido derivatives and was inclined to accept the Collie formula. The results of Stollé, however, have been confirmed in the past year by E. Benary[4] and the evidence gained through the phenylhydrazine reaction shown to conform with the Feist formula.

There is no doubt therefore but that the formula for dehydroacetic acid rests upon one of these two possible structures, with the more recent evidence favoring somewhat the Feist hypothesis. Granting for the time that the Collie formula may be the correct one, it seemed that we might have an excellent means of confirming the presence of an acetonyl group in this acid by studying its reaction with nitromalonic aldehyde. Sodium nitromalonic aldehyde has a marked tendency to condense with all derivatives containing the group $—CH_2.CO.CH_2—$, and this often without the presence of condensing agents. The work of Hill and his coworkers[5] indicates what the trend of the reaction between this aldehyde and dehydroacetic acid would be, were the Collie hypothesis correct,



XIV.

When one of the substituents in the acetone group is strongly negative, a greater concentration of alkali or condensing agent may be required,[6] hence the negative character of the oxypyrone group could well be looked after. In all cases the action of nitromalonic aldehyde upon dehydroacetic acid, as well as dehydroacetocarboxylic acid, failed to give any condensation product. Though the conditions were varied between great extremes no positive results could be obtained. Now the hydrated salts of dehydroacetic acid have been represented by Collie[7] as having a formula such as $CH_3.CO.CH_2.CO.CH_2.CO.CH_2.COONa$, and by loss of one molecule of water passing over into that type as given by Collie for dehydro-

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[1] *J. Chem. Soc.*, **59**, 607, 617 (1891); *Ibid.*, **77**, 976 (1900).

[2] *Ber.*, **38**, 3026 (1905).

[3] *Ibid.*, **41**, 4161 (1908).

[4] *Ibid.*, **43**, 1070 (1910).

[5] *Am. Chem. Jour.*, **22**, 89 (1899); *Ibid.*, **24**, 1 (1900); *Ibid.*, **33**, 1 (1905).

[6] Hale and Robertson, *Am. Chem. Jour.*, **39**, 680 (1908).

[7] *J. Chem. Soc.*, **77**, 974 (1900).

acetic acid in its enolic form (V). Such an arrangement of acetonyl groups, as thus pictured by Collie, would offer several possibilities for a ready condensation with nitromalonic aldehyde; but, as just stated, the absence of any condensation whatsoever with this most reactive substance points conclusively to the non-existence of the nucleus, —$CH_2.CO.CH_2$—, or the tautomeric form with which it may be in equilibrium; the presence of the latter is found not to interfere with the final result in these condensations. Similarly the action of nitromalonic aldehyde upon dehydrobenzoylacetic acid, as well as dehydropropionylacetic acid, netted no positive results. Upon this purely negative evidence we are inclined to accept the Feist formula as the correct one and have applied further tests to confirm this conclusion.

The action of benzaldehyde, for example, was studied with a view of determining the possible condensation under the influence of acid or alkali. From the observations of Goldschmiedt,[1] Harries and others[2] it has been pointed out that aromatic aldehydes react with saturated unsymmetrical ketones in two different ways: preferably with the methyl group of the ketone in the presence of alkali, and with the methylene group in the presence of acid. Stoermer and Wehln[3] further showed, from a study of phenoxylacetone and benzaldehyde, that the course of this condensation is largely dependent upon the nature of the substituent groups. The more strongly acid the radicle adjacent to the methylene group, the more reactive will this methylene group become and, as a consequence, the more likely it is alone to react with aromatic aldehydes under all conditions of condensation, *i. e.*, whether the solution is acid or alkaline. The example of acetoacetic ester, with its strongly negative carbethoxyl adjacent to the methylene group, in giving only the compound benzylidene acetoacetic ester,[4] $CH_3.CO.C : (CHC_6H_5).COOC_2H_5$, under the influence of alkali as well as acid is thus well accounted for. Phenoxylacetone, $C_6H_5O.CH_2.CO.CH_3$, condenses with one molecule of benzaldehyde in either acid or alkaline solution to give only the benzylidene phenacetol, $C_6H_5O.C(:CHC_6H_5).CO.CH_3$. When this methylene group is once involved, the remaining methyl group may, in some cases of which this is one, be made to combine with a second molecule of benzaldehyde. The analogy between acetoacetic ester and phenoxylacetone lies, therefore, in the negative character of the carbethoxyl and phenoxyl groups; the latter, however, is not so negative as the former and yet much more so than the phenyl group, as just cited in the studies of Goldschmiedt.

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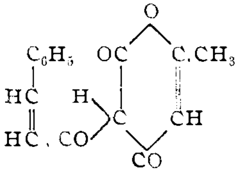
[1] *Monatsh.*, **18**, 437 (1897); **19**, 461 (1898); **22**, 659 (1901).

[2] *Ber.*, **35**, 966 (1902); *Ibid.*, **35**, 3088 (1902).

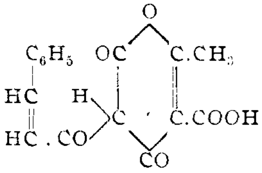
[3] *Ibid.*, **35**, 3549 (1902).

[4] *Ibid.*, **14**, 347 (1881); *Ibid.*, **29**, 172 (1896); *Ann.*, **218**, 177 (1883); *Ibid.*, **281**, 63 (1894).

If we now look upon the formulas assigned to dehydroacetic and dehydroacetocarboxylic acids by Collie on the one hand, and by Feist upon the other, we may draw certain conclusions which these studies with benzaldehyde should lead us to expect. Since benzaldehyde has a tendency to condense with a methylene or methyl group only when adjacent to a carbonyl group, Feist's formula for these acids could give for each only one possible product: benzylidene dehydroacetic acid (XV) and benzylidene dehydroacetocarboxylic acid (XVI):



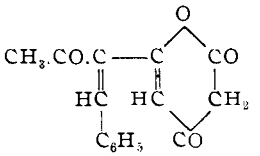
XV.



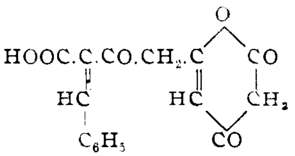
XVI.

These condensations should proceed easily when the aldehyde and the acid are brought together in alkaline solution. The work of Harries and others has indicated the trend of just such a condensation when a methyl group is present. The absence of a methylene group may be expected to make possible any condensation with a methyl group when the solution is alkaline, and again it must reduce to a minimum any chance for this methyl group to enter into condensation when the solution is acid.

In the consideration of Collie's formulas for these two acids the acetonyl group, as the side chain, would offer only two possibilities. For dehydroacetic acid we probably should have only one molecule of benzaldehyde entering into reaction in the acetone nucleus, and this with the methylene group alone, owing to the acid character of the pyronone ring as the substituent (XVII). This condensation, however, should proceed in acid solution, whereas in alkaline solution the same end result would



XVII.



XVIII.

be obtained. It is doubtful whether or not the methyl group of this side chain could be made to enter into condensation. If possible it would react in alkaline solution. Now in addition to this acetone nucleus there is a methylene group in the pyronone ring and here, as elsewhere, the tendency would naturally be for benzaldehyde to condense easily in acid solution (if not also in alkaline solution).

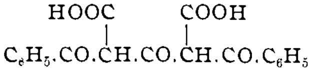
For dehydroacetocarboxylic acid Collie accounts for the carboxyl on the end of the acetonyl chain. In other words he reproduces the exact conditions that are present in acetoacetic ester, where a methylene group is adjacent to a strongly negative or acid group. The tendency therefore must be that benzaldehyde will condense most readily with this particular methylene group in acid solution. In alkaline solution, also, the same product should result (XVIII). Whether the second methylene group, adjacent to the ring, or the methylene group in the ring is also involved need not concern us; the conditions, however, certainly favor the condensation with a second molecule of benzaldehyde.

The facts are that dehydroacetic acid, as well as dehydroacetocarboxylic acid, condenses with only one molecule of benzaldehyde in alkaline solution. In acid solution dehydroacetocarboxylic acid refuses altogether to condense with this aromatic aldehyde and dehydroacetic acid, if at all, condenses with benzaldehyde in acid solution in only the very smallest degree. This absence of condensation in acid solution forces us to the conclusion that in dehydroacetocarboxylic acid there can not possibly be a methylene group adjacent to a carboxyl as is demanded by the Collie formula. The analogy with acetoacetic acid breaks down completely in this instance. Again in dehydroacetic acid itself the absence of any condensation product in acid solution, other than a small amount of the same product as is obtained in alkaline solution, shows that the methylene groups as here demanded by the Collie formula are entirely without activity—a supposition hardly warranted by the exhaustive and careful studies of Harries and others upon the ease with which aromatic aldehydes enter into condensation with these groups.

According to the formula assigned to dehydrobenzoylacetic acid in accordance with the Feist hypothesis (IX) a condensation of this acid with benzaldehyde would not be possible, a conclusion substantiated by the experimental results, whereas according to the Collie formula for this acid (XIII) we have just that condition which should be most favorable for condensation of methylene groups with benzaldehyde, especially in acid solution. Herein is further proof that Feist's form la alone stands in full agreement with the facts observed.

In order now to attack the problem from the constructive point of view it was thought best to try out v. Pechmann's hypothesis and ascertain, if possible, the exact course of the reaction between acetic anhydride and acetonedicarboxylic acid. If this reaction proceeds in the manner outlined by v. Pechmann and all chances for a condensation in accordance with the plan outlined by Collie, to yield an acid of the structure he proposed, were eliminated, then it would appear that a most conclusive proof of the Feist formula is at hand.

When benzoic anhydride is made to replace acetic anhydride in the v. Pechmann reaction a beautifully crystalline product is obtained. This may be prepared also by the action of benzoyl chloride in place of the anhydride. The product is a symmetrical dibenzoylacetonedicarboxylic acid (XIX). It possesses two carboxyl groups and four ionizable hydrogen atoms. Unfortunately the compound undergoes decomposition upon heating (even before melting) and can not be made to pass over into a dehydrobenzoylacetocarboxylic acid (analogy with the hypothetical diacetylacetonedicarboxylic acid, see (VI)) as was expected. For this result, of course, a partial tautomerization into the enolic form would be a prerequisite, and were it possible to heat the compound for any length of time without complete decomposition, such a result may well be anticipated.



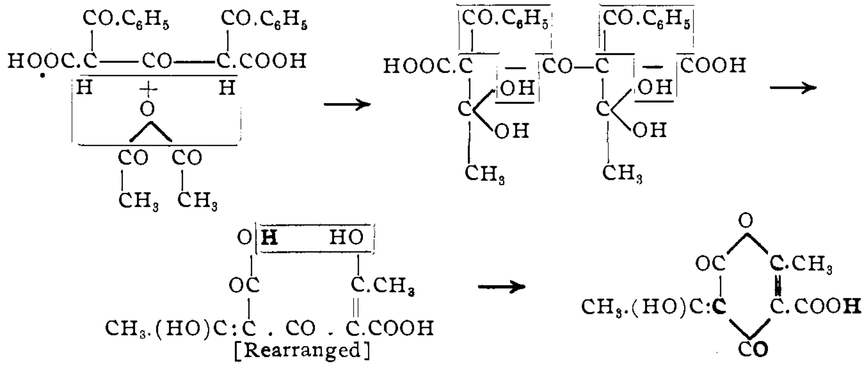
$$C_6H_5.CO.\overset{\text{HOOC}}{\overset{|}{C}}H.CO.\overset{\text{COOH}}{\overset{|}{C}}H.CO.C_6H_5$$

XIX.

The action of dry hydrogen chloride upon this product dissolved in absolute alcohol gives the diethyl ester. This ester is acid in character with two ionizable hydrogen atoms. There can be no doubt as regards the structure of either the acid or its diethyl ester. Even by gentle heating the ester also undergoes ready decomposition and shows no tendency to condense into a dehydrobenzoylacetocarboxylic acid, as might be inferred from the action of heat upon benzoylacetic ester. A warm barium hydroxide solution hydrolyzes the ester, or the acid, into the constituents—benzoic acid and free acetonedicarboxylic acid. With too strong acid or alkali complete decomposition ensues.

By the use of benzoacetic anhydride in place of benzoic anhydride it was thought possible to favor this partial tautomerization, through the presence of one acetyl group, if such takes place as described in the case of acetic anhydride itself when acting upon acetonedicarboxylic acid. The product, however, is so extremely unstable that no positive results as yet have been obtainable.

Various means were then brought to bear upon the dibenzoylacetonedicarboxylic acid with the hope of effecting some partial condensation, at least, within its molecule, but in no case was such a result accomplished. Quite unexpectedly it was found that the action of acetic anhydride upon this dibenzoylacetonedicarboxylic acid yielded the dehydroacetocarboxylic acid of v. Pechmann. A long boiling is necessary when the anhydride alone is employed, but with the addition of a drop or two of conc. sulfuric acid the action is complete in a very few minutes. The diethyl ester does not react with acetic anhydride. We have, therefore, in this reaction a key to the mechanism of the reaction of acetic anhydride upon acetonedicarboxylic acid. Just as the benzoyl groups attach themselves to the acetone nucleus so also must the acetyl groups arrange themselves in this same molecule—one acyl group replacing a hydrogen atom in each of the two methylene groups. In considering the action of acetic anhydride upon the dibenzoyl derivative we may construe it as a repetition of the symmetrical condensation in which now the two single hydrogen atoms of the methine groups are replaced by acetyl and then, through addition of water and conversion into the enolic form, benzoic acid is split off and dehydroacetocarboxylic acid at once produced:



More simply, perhaps, we may look upon the action as merely one of replacement of benzoyl by acetyl groups and final condensation of the exceedingly unstable diacetyl derivative into its δ-lactone or dehydroacetocarboxylic acid. The slowness of this action in the presence of acetic anhydride alone confirms the belief that the acetyl groups must eventually supplant the benzoyl groups.

Though the dibenzoylacetonedicarboxylic acid could not be raised to a temperature at which tautomerization and finally intramolecular condensation was possible, this replacement of the two benzoyl groups, of known position, by acetyl groups, just prior to their entering into the tautomeric form and final condensation of the molecule into dihydroacetocarboxylic acid, offers conclusive proof on the conditions which underlie the v. Pechmann reaction. As still further proof, in substantiation of this explanation, the action of propionic anhydride upon dibenzoylacetonedicarboxylic acid is found to give most readily the corresponding dehydropropionylacetocarboxylic acid (VII) of v. Pechmann m. 114–5°.[1]

According to the plan outlined by Collie (see above) there can be no possible condensation of benzoylchloride, or benzoic anhydride, with acetonedicarboxylic acid. In fact the only chance for benzoic anhydride to enter here into condensation, leaving the two carboxyl groups free, is in accordance with Feist's hypothesis. We may assume then once for all that it is the halogen of benzoyl chloride, or the anhydride oxygen of benzoic anhydride, that actually enters directly into reaction with the acetone nucleus. The compound formed is exceedingly unstable

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[1] *Ann.*, 273, 201 (1893).

when one or two acetyl groups constitute the entering factors, passing over in the latter case into its δ-lactone, a derivative of dehydroacetic acid.

Investigations upon other anhydrides in this connection have been undertaken, particularly the study of phenylacetic anhydride. The general mechanism of the reaction, however, remains the same and stands out conclusively in support of v. Pechmann's interpretation of this condensation—a proof amply sufficient to estabish Feist's formula as the only possibility for dehydroacetic acid.

Experimental Part.

Acetonedicarboxylic acid[1] was converted into dehydroacetocarboxylic acid (m. 154°) and finally into dehydroacetic acid (m. 109°) according to the method of v. Pechmann.[2] It was found that a drop or two of conc. sulfuric acid or anhydride, when added to the reaction mixture of acetic anhydride containing acetonedicarboxylic acid, materially hastened the transformation into dehydroacetocarboxylic acid and at the same time insured the maximum yield.

Attempts at Condensation with Sodium Nitromalonic Aldehyde.—If Collie's hypothesis is the correct one, then the condensation with nitromalonic aldehyde should proceed with great ease and a product of the constitution as shown in formula (XIV) would be produced. This substance, if formed, would give by oxidation the well-known *m*-nitro-*o*-hydroxybenzoic acid. Solutions of dehydroacetic acid containing from one to ten molecules of sodium hydroxide, $N/10$ solution, were allowed to stand a number of days with sodium nitromalonic aldehyde in equimolecular quantities. A slight red coloration usually made its appearance, but in all cases upon acidification the original weight of dehydroacetic acid was recovered. Piperidine, diethylamine, and other condensation agents were employed but always with negative results. In a similar manner, only negative results were obtained from attempts to condense dehydroacetocarboxylic acid with nitromalonic aldehyde.

Benzylidene Dehydroacetocarboxylic acid, $C_{16}H_{12}O_6$ (XVI).—Two grams of dehydroacetocarboxylic acid were dissolved in 50 cc. of water and 7 cc. of 2 N sodium hydroxide solution added to alkaline reaction. Two grams of freshly distilled benzaldehyde were then admitted and the flask set in a shaker for two or three days. The contents of the flask were then extracted with ether to remove the excess of benzaldehyde and the aqueous solution acidified with hydrochloric acid, upon which the lemon-yellow benzylidene was precipitated. The weight of the dry product was 2.2 grams. Benzylidene dehydroacetocarboxylic acid is insoluble in water; only slightly soluble in ether, but readily soluble in chloroform, benzene,

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[1] *Ann.*, **261**, 155 (1891).

[2] *Ber.*, **24**, 3600 (1890); *Ann.*, **273**, 186 (1893).

acetic ester, or acetone. It is fairly soluble in hot ligroin, crystallizing out on cooling, and quite soluble in hot alcohol from which it crystallizes best in the form of needle clusters. The product melts at 147–8° (cor.). Upon sublimation, twice or three times repeated, it gives dehydroacetic acid m. 109°.

The action of benzaldehyde upon dehydroacetocarboxylic acid in acid solution failed to give either this benzylidene or any other condensation product. The dehydroacetocarboxylic acid was dissolved in benzaldehyde and treated with dry hydrogen chloride in the cold and the mixture allowed to stand a week or more. Again the acid was dissolved in chloroform, and also in benzene, and into each of these solutions containing benzaldehyde in excess, the introduction of dry hydrogen chloride was unproductive of results. In all cases the unacted-upon dehydroacetocarboxylic acid was recovered.

In the crystallization of the benzylidene compound from alcohol considerable care must be used, as slight traces of alkali that may still be present work toward its rapid decomposition in alcoholic solution.

Calculated for $C_{16}H_{12}O_6$: C, 63.98; H, 4.03.
Found: C, 63.71; H, 4.31.

Benzylidene Dehydroacetic Acid, $C_{15}H_{12}O_4$ (XV).—Into a solution containing 2 grams of dehydroacetic acid in 80 cc. of water 6 cc. of 2 *N* sodium hydroxide solution were added to alkaline reaction. Two grams of freshly distilled benzaldehyde were then admitted to the flask and the latter set in a shaker for two or three days. The contents of the flask were then extracted with ether to remove free benzaldehyde and the aqueous residue acidified, whereupon the light yellow benzylidene compound was precipitated. Benzylidene dehydroacetic acid is extremely soluble in benzene, alcohol, acetic ester, chloroform, acetone, or ether. It is fairly soluble in hot ligroin, from which it separates in poorly defined crystals, and fairly soluble in hot water, crystallizing best from this solution in irregular needle clusters, almost colorless and melting at 105–6° (cor.). By sublimation this benzylidene compound passes back readily into dehydroacetic acid.

Calculated for $C_{15}H_{12}O_4$: C, 70.30; H, 4.68.
Found: C, 70.12; H, 4.91.

The action of dry hydrogen chloride upon a mixture of benzaldehyde and dehydroacetic acid in a cold chloroform solution was unproductive of results. When dehydroacetic acid is dissolved in the benzaldehyde and a current of dry hydrogen chloride led through the reaction mixture a slight change is noted. If this mixture, after standing several days, is neutralized with sodium hydroxide solution and all excess of benzaldehyde removed by shaking with ether, the addition of hydrochloric acid will precipitate a slightly yellow colored compound which consists of a mixture of dehydroacetic acid and the benzylidene derivative of this acid just described. It is probable that the alkali added above may have facilitated the formation of this product, and again it is not unlikely that the pyronone group of dehydroacetic acid is sufficiently acid to interfere in any appreciable way with the formation of the regular benzylidene compound described above, even in acid solution.

s-Dibenzoylacetonedicarboxylic Acid, $C_{19}H_{14}O_7$ (XIX). — The crude acetonedicarboxylic acid obtained by the method of v. Pechmann[1] and still somewhat moist with sulfuric acid may advantageously be used in this work. A flask containing 32 grams of benzoic anhydride is set upon a steam bath and into the molten anhydride 4 grams of acetonedicarboxylic acid are added with vigorous stirring. Solution takes place rapidly, but no less benzoic anhydride than eight times the weight of acetonedicarboxylic acid will serve for a clear solution. The color of the reaction-mixture becomes at first a yellow but passes into a dark red in a very few minutes. Considerable heat is given out by the reaction itself. After 2 or 3 minutes the action is at an end. A little ether is now added to the flask (care being taken to keep flask closed during this step to avoid loss) until the reaction-mixture is increased to twice its original volume and the contents of the flask appear as a homogeneous mixture. Into the flask, with its contents still warm, an excess of ether (equal in volume to that of the total reaction-mixture) is now poured when as a result a yellow semi-crystalline substance will be precipitated. The contents of the flask are now poured out upon a suction filter and the precipitate washed with warm ether. The ether serves to remove the large excess of benzoic anhydride and acid. From the ether mother liquors a considerable quantity of benzoic anhydride may be recovered. The precipitate, however, still contains a small amount of these impurities. Its purification is easily effected by solution in hot benzene from which the almost pure dibenzoylacetonedicarboxylic acid separates immediately. From the benzene mother liquor, evaporated to dryness and washed with ether, a small quantity of the dibenzoyl derivative may be procured. From the 4 grams of crude acetonedicarboxylic acid 1.9 grams of the pure product were obtained.

In place of benzoic anhydride somewhat less of benzoyl chloride will suffice for this same reaction. The operation is carried out in an exactly analogous manner, but much more disagreeably to the operator.

s-Dibenzoylacetonedicarboxylic acid is insoluble in water, ligroin, carbon tetrachloride or ether; soluble in cold acetone or acetic ester; and fairly soluble in hot chloroform, glacial acetic acid, alcohol or benzene, crystallizing from each upon cooling, but more easily from the last named.

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[1] *Loc. cit.*

It appears in the form of colorless leaflets when pure, melting at 162° (cor.) with decomposition slightly below this point.

Calculated for $C_{19}H_{14}O_7$: C, 64.39; H, 3.98.
Found: C, 64.43; H, 4.23.

When titrated 0.0930 gram substance required 10.2 cc. *N*/10 NaOH solution. Calculated for 4 molecules of NaOH 10.5 cc. should have been used. Hence the presence of 4 ionizable hydrogen atoms. From these neutral and very dilute solutions, hydrochloric acid will reprecipitate the dibenzoyl derivative unchanged. Mild alkalies easily saponify this compound, giving benzoic acid and acetonedicarboxylic acid.

When this dibenzoylacetonedicarboxylic acid is subjected to heat, carbon dioxide is evolved at a very early stage and benzoic acid sublimes from the molten mass shortly afterwards. When the compound is dissolved in acetic anhydride and then submitted to heat no apparent action takes place, but if the solution is boiled a change of color is noticed and the benzoyl groups are gradually replaced by the acetyl groups with the subsequent formation of dehydroacetocarboxylic acid. This end is brought about almost immediately if a few drops of concentrated sulfuric acid are added to the acetic anhydride solution and the mixture warmed upon the steam bath. When the deep red color is developed (after 4 or 5 minutes) water is gradually added to the mixture and the yellow glistening flakes of dehydroacetocarboxylic acid (m. 154°) of v. Pechmann appear. There can be no doubt but that the acetyl actually replaced the benzoyl groups. The mother liquor showed the presence of benzoic acid as was expected.

From attempts at heating dibenzoylacetonedicarboxylic acid in molten benzoic anhydride with a view to making possible the condensation into dehydrobenzoylacetocarboxylic acid, without this tendency for replacement of the benzoyl groups present, no definit results have been obtained. Decomposition, of course, set in early with an evolution of carbon dioxide. Dry hydrogen chloride was without action upon this dibenzoyl derivative dissolved in benzene as well as in other anhydrous solvents.

If dibenzoylacetonedicarboxylic acid is dissolved in propionic anhydride and the solution, after the addition of a drop of sulfuric acid, warmed upon a steam bath, the complete replacement of the benzoyl by propionyl groups is effected. The product obtained by dilution of the reaction-mixture is the crystalline dehydropropionylacetocarboxylic acid of v. Pechmann, melting at 114–5°.

Diethyl Ester of s-Dibenzoylacetonedicarboxylic Acid, $C_{23}H_{22}O_7$ (see XIX).—A stream of dry hydrogen chloride is passed into a flask, set in freezing mixture, and containing 3 grams of dibenzoylacetonedicarboxylic acid suspended in 8 or 9 times its weight of absolute alcohol. When complete saturation is reached and solution effected, the flask is corked and set aside in cool place over night. The clear red solution is then poured into a beaker containing cracked ice, and after an hour or more the needle-like crystals filtered off and dried upon a porous plate. The mother liquor should be extracted with ether several times and the ether solutions evaporated to small bulk, dried with calcium chloride, and then freed of ether by warming over a steam bath. When cool the introduction of a crystal of the crude product, as filtered off above, will usually start crystallization. The entire crystalline mass dried upon a porous plate weighed 1.8 grams. When dissolved in benzene with the addition of a small quantity of ligroin there soon appeared beautiful long needles of the pure, colorless diethyl ester m. 70.5° (cor.). This diethyl ester is almost insoluble in water but extremely soluble in acetic acid, acetone, alcohol, chloroform, acetic ester or benzene; it is fairly soluble in hot ligroin, from which it crystallizes in needle clusters upon cooling. The best means of purification consists in dissolving the ester in a small quantity of benzene and adding ligroin to this clear solution; almost immediately the large needle clusters appear.

Calculated for $C_{23}H_{22}O_7$: C, 67.28; H, 5.40.
Found: C, 67.20; H, 5.67.

In a molecular weight determination in benzene solution,

I. 0.1754 gram substance in 17.40 grams benzene caused a depression of 0.116° in the freezing point of solvent.

II. 0.2593 gram substance in 17.40 grams benzene caused a depression of 0.170° in the freezing point of solvent.

Calculated for $C_{23}H_{22}O_7$: Mol. wt., 410.16; Found: I, 417.1 and II, 420.8.

For titration with N/10 sodium hydroxide solution (phenolphthalein as indicator). 0.1230 gram substance required 6.2 cc. of this alkaline solution. Calculated for 2 molecules of NaOH, 6 cc. should have been used. Hence the presence of two ionizable hydrogen atoms is shown.

This diethyl ester is in fact quite acid in its reactions, as may be inferred at once from the position of the hydrogen atoms on the carbon atoms adjacent to these carbonyl groups. From its dilute neutral solutions hydrochloric acid will reprecipitate the ester unchanged.

By the application of heat the ester, after melting, undergoes ready decomposition with the liberation of benzoic acid. No condensation product was detected in the charred mass.

Acetic anhydride is without action upon this ester just as v. Pechmann reported true for the diethyl ester of acetonedicarboxylic acid.

When boiled with a barium hydroxide solution the diethyl ester is readily saponified. After the hot mixture is filtered, acidification of the filtrate and extraction with ether gave crystals of benzoic acid. From the precipitate, taken up in hydrochloric acid and extracted with ether, was obtained the white crystals of the original acetonedicarboxylic acid, m. 135°.

The Action of Benzoacetic Anhydride upon Acetonedicarboxylic Acid.—This anhydride was prepared to the method of Gerhardt[1] but is difficult to obtain in a high degree of purity. When acetonedicarboxylic acid is dissolved in this anhydride, warmed upon a steam bath, immediate action ensues. After a few minutes the red colored product was mixed with ether in excess and the undissolved portion filtered off. This precipitate, however, can not be dried, owing to its great tendency for decomposition. It may be preserved under ether for a short time. Several attempts were made to bring about a condensation in its molecule—supposedly a benzoylacetylacetonedicarboxylic acid—to form a benzoyl methylpyronone derivative of similar structure to dehydroacetic acid. No positive results, however, were obtained, and owing to the difficulty in securing what may be called the pure benzoacetic anhydride, no further work was attempted in this direction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE FORMATION OF BENZALDEHYDE AND 2,4,6-TRIBROMOANILINE FROM 3,5-DIBROMO-4-AMINOBENZHYDROL BY THE ACTION OF BROMINE.

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While engaged on the study of certain bromine derivatives of 4-aminobenzophenone and 4-aminobenzhydrol, the following experiment was performed.

Five grams of 4-aminobenzhydrol (prepared by reducing 4-aminobenzophenone with sodium amalgam in alcoholic solution)[2] were dissolved in 150 cc. of washed and dried chloroform and to the solution 4 grams (two atoms) of bromine were added. A precipitate was thrown down and soon clotted together to form what appeared under a magnifying glass as a mixture of yellowish crystals and a yellow tarry mass. This precipitate was filtered off but could not be made to yield a crystalline substance—water, ether, acetone, naphtha, benzene, ethyl alcohol, chloroform, glacial acetic acid and ethylene dibromide were tried in vain. The material was soluble in alcohol and when the latter was evaporated off, a dark yellow jelly remained which had the odor of benzaldehyde. No pure products could be obtained but this was probably due to the presence of an anhydride of high molecular weight, identical with or analogous to that described by Kippenberg,[3] and formed from 4-aminobenzhydrol by the action of hydrobromic acid. In our case hydro-

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[1] *Ann.*, 87, 81 (1853).

[2] Kippenberg, *Ber.*, 30, 1135.

[3] *Ibid.*, 30, 1137, 1138.