XXXII.—*Benzoylactic Acid and some of its Derivatives.* Part II.

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IN Part I of this research (Trans., 1884, 170), I described the preparation and properties of ethylic benzoylacetate and of benzoylactic acid, as well as of some compounds in which the hydrogen-atoms of the methylene group of the former are displaced by alcoholic radicles, such as ethyl-, diethyl-, and allyl-benzoylactic ether, together with the products of their hydrolysis. Before describing the more complicated reactions in which ethylic benzoylacetate takes part, I should like to give the results of the experiments I have made with some of these compounds since the publication of Part I (Trans., 1884, 170).

It has been found that although the substituted etheric salts of the benzoylactic acids cannot be distilled without decomposition under the ordinary pressure, they can easily be obtained pure by distillation under diminished pressure. Using an apparatus similar to that described by Thorne, I have succeeded in purifying the monethyl- and allyl-derivatives described in the previous paper. If the crude product of the action of ethyl iodide on ethylic benzoylacetate is distilled under a pressure of 225 mm., a small quantity of acetophenone passes over first, and then the temperature rises rapidly to 220°, between which and 240° nearly the whole comes over as an almost colourless oil, leaving but a small residue. On repeatedly refractioning this oil under the same pressure, it distils mostly between 230—235°. The portion used for analysis boiled at 231—232° at 225 mm.

0.1550 gram substance gave 0.1020 gram H_2O and 0.4016 gram CO_2 .

	Found.	Theory. $C_6H_5.CO.CH(C_2H_5).COOC_2H_5.$
C	70.66 per cent.	70.91 per cent.
H	7.31 ,,	7.27 ,,
O	22.03 ,,	21.82 ,,

Ethylic ethylbenzoylacetate is a colourless, strongly refracting oil possessing an aromatic odour and burning taste. When pure, it appears to distil at the ordinary pressure almost without decomposition. The boiling points of the pure substance were incidentally noticed as being—

210—211°	at	90 mm.
223—224	„	150 ,,
231—232	„	225 ,,

Ethylic ethylbenzoylacetate is insoluble in potassic hydroxide solution, but appears to give a sodium compound on mixing it with sodic ethoxide. On continued boiling, no condensation-product is formed corresponding with the dehydrobenzoylactic acid, which is so easily obtained by heating ethylic benzoylacetate for a short time by itself. This reaction I hope to describe in Part III of this paper. Ethylic acetoacetate and ethylacetoacetate behave in a precisely similar way. On passing ethylic acetoacetate through a tube at a dull red heat, it is almost completely decomposed, yielding as much as 20 per cent. of its condensation-product, dehydracetic acid, whereas ethylic ethylacetoacetate passes through almost unaltered, no trace of the analogous acid being formed.

Ethylic allylbenzoylacetate may also be purified in exactly the same way as ethylic ethylbenzoylacetate. On submitting the crude product of the action of allyl iodide on ethylic benzoylsodacetate to distillation under a pressure of 225 mm., nearly the whole passes over between 225—245° as a peculiar greenish-coloured oil, with a slight reddish fluorescence. This coloration can only be removed by repeated fractioning, and even then it often returns on standing.

Pure ethylic allylbenzoylacetate boils at—

220°	under	100 mm. pressure.
226—227°	„	130 ,, ,,
240—241	„	225 ,, ,,

As it is difficult to burn, it is necessary that the combustion should be done with chromate of lead. The following numbers were obtained :—

0.1491 gram substance gave 0.0902 gram H_2O and 0.3924 gram CO_2 .

	Found.	Theory. $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{CH}:\text{CH}_2)\cdot\text{COOC}_2\text{H}_5$.
C	71.77 per cent.	72.41 per cent.
H	6.72 ,,	6.89 ,,
O	21.51 ,,	20.69 ,,

Ethylic allylbenzoylacetate possesses the peculiar disagreeable odour characteristic of most allyl compounds. It does not solidify at 0° . The solution in acetic acid takes up bromine readily, especially if warmed, and without evolution of hydrobromic acid.

Ethylic benzoylacetate itself cannot be purified by distillation under diminished pressure, the greater part being decomposed, owing to the comparative slowness with which distillation takes place. When distilled as rapidly as possible (at 200 mm.) a portion passes over between 220 — 225° , consisting of nearly pure ethylic benzoylacetate, but a large residue is left containing considerable quantities of dehydrobenzoylactic acid.

Having obtained ethylic monethyl- and allyl-benzoylacetates in a pure state, it was next thought necessary to repeat the hydrolysis with potash, in order, if possible, to obtain the acids in a pure state, but even when very dilute alcoholic potash was used, the acids were always mixed with benzoic acid, in some cases to a very considerable extent.

It was then thought that hydrolysis with sulphuric acid might give better results, and several experiments were therefore tried, using ethylic benzoylacetate itself in the first case.

On mixing ethylic benzoylacetate with 20 times its volume of concentrated sulphuric acid, and allowing it to remain for some time, the mixture becomes thick and dark-coloured, small quantities of carbonic anhydride and sulphurous anhydride being given off.

After standing for 14 days, the product was poured into ice water; this caused the precipitation of a thick dark brownish oil, which partly solidified on prolonged agitation. This uninviting body was separated from the aqueous solution by filtration, washed well with water, and then spread out on a porous plate; in this way the dark brown oil was almost completely removed from the crystals in two or three days, leaving them as a hard yellowish crystalline crust. After recrystallising it several times from warm benzene, the substance was easily obtained pure, melting between 103 — 104° , and presenting all the appearance of benzoylactic acid.

On adding a drop of ferric chloride to the alcoholic solution, it gave the beautiful violet coloration mentioned in Part I, and the acid itself on dry distillation split up quantitatively into carbonic anhydride and acetophenone. There can be no doubt, therefore, that the substance was pure benzoylactic acid. Experiments were next tried

to ascertain if ethylic ethylbenzoylacetate could also be hydrolysed in the same way. A small quantity of this ethereal salt was mixed with nearly three times its volume of concentrated sulphuric acid, and allowed to remain for three weeks. The solution became brownish-coloured, but not nearly so dark as in the case of ethylic benzoylacetate itself; on adding water, an almost colourless oil was precipitated, which was removed by shaking with ether, and on evaporating the ether, a yellowish oil remained behind; this when exposed over sulphuric acid in a vacuum, deposited crystals, apparently ethylbenzoylacetic acid. The quantity, however, was unfortunately too small for analysis, so that it will be necessary to repeat the experiment with more material before I can be certain that this method is of general application for the hydrolysis of ethylic benzoylacetate derivatives.

Part II of this research comprises the preparation and properties of ethylic nitrosobenzoylacetate, dibenzoylacetic acid, di- and tri-benzoylmethane, the reduction of ethylic benzoylacetate, the action of phosphorous pentachloride on ethylic benzoylacetate, and the condensation of the latter with benzaldehyde.

Ethylic Benzoylnitrosoacetate.

By the action of nitrous acid on ethylic acetoacetate, Victor Meyer obtained ethylic nitrosoacetoacetate, according to the equation—

After a series of admirable researches, he proved that the formula of this compound was not $\text{CH}_3\text{CO}\cdot\text{CH}(\text{NO})\cdot\text{COOC}_2\text{H}_5$, and therefore did not contain the nitroso-group NO, as was at first supposed, but that it was in reality an isonitroso-body, having the constitution $\text{CH}_3\text{CO}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{COOC}_2\text{H}_5$, and containing the isonitroso-radicle : N.OH.

With the exception of ethylic malonate, ethylic acetoacetate is the only compound which is capable of being converted into an isonitroso-derivative; for the substituted acetoacetates, such as ethylic ethylacetoacetate, $\text{CH}_3\text{CO}\cdot\text{CH}(\text{C}_2\text{H}_5)\cdot\text{COOC}_2\text{H}_5$, possessing only one hydrogen-atom which is capable of being substituted by any group, cannot combine with the dyad radicle NOH.

The nitroso-derivative of the whole molecule is therefore never formed by the action of nitrous acid on such bodies, but the ethereal salt being first hydrolysed, carbonic anhydride is given off, and the nitroso-ketone remains behind :—

It therefore appeared interesting to try the action of nitrous acid on ethylic benzoylacetate and some of its derivatives, in order to determine whether they would follow the same law or not.

After several trials, the following was found to be the best method of preparing ethylic nitrosobenzoylacetate:—

Ethylic benzoylacetate is first dissolved in dilute sodic hydroxide solution, filtered, mixed with an excess of sodic nitrite, and cooled down below 0° in a freezing mixture. Dilute sulphuric acid is then slowly added from a burette until the mixture is decidedly acid, care being taken that the liquid does not get warm. After a short time, more sodic hydroxide solution is added; this dissolves all that was precipitated by the sulphuric acid, producing an intense yellow solution, a sign that a nitroso-body has been formed. Last of all, the ethylic nitrosobenzoylacetate is precipitated by adding an excess of sulphuric acid. It separates as an oil, which, however, on agitating soon solidifies to long colourless needles. These are collected, well washed with water, and separated from any oily matter by spreading them out on a porous plate. In order to purify it, it is dissolved in a little hot alcohol, and water added until it becomes milky. The whole is then warmed up again and allowed to stand, when pure ethylic nitrosobenzoylacetate separates out in beautiful long colourless needles; on analysis, these gave the following numbers:—

- I. 0.1711 gram substance gave 0.0813 gram H_2O and 0.3729 CO_2 .
 II. 0.1566 gram substance gave 0.0730 gram H_2O and 0.3423 gram CO_2 .
 I. 0.2617 gram substance gave 16 c.c. N, bar. = 718 mm., $t. = 21^{\circ}$.
 II. 0.2154 " " 12.5 c.c. N, bar. = 716 mm., $t. = 18^{\circ}$.

	Found.		Theory. $C_{11}H_{11}NO_4$.
	I.	II.	
C	59.44	59.62 per cent.	59.73 per cent.
H	5.28	5.18 "	4.97 "
N	6.56	6.31 "	6.33 "
O	28.72	28.89 "	28.96 "

From its analogy to ethylic nitrosoacetoacetate, this compound must have the formula $C_6H_5.CO.C(N.OH).COOC_2H_5$.

Ethylic nitrosobenzoylacetate melts at $120-121^{\circ}$. It is easily soluble in alcohol, ether, benzene, and chloroform, sparingly in water. It dissolves easily in alkalis, forming a yellow solution like all nitroso-bodies, and on acidifying is reprecipitated unchanged. It is decomposed by dry distillation with separation of charcoal and formation

of hydrocyanic acid. A heavy oil passes over, which soon solidifies, and then melts at $110-114^{\circ}$; it is perhaps impure benzoic acid.

On treating ethylic nitrosoacetoacetate with alkalis, it is decomposed in the same way as ethylic acetoacetate itself, yielding nitrosoacetone instead of acetone. It was thought likely, therefore, that ethylic nitrosobenzoylacetate under the same conditions would give nitrosoacetophenone.

In order to test this, 3 grams of ethylic nitrosobenzoylacetate were dissolved in dilute potash, and allowed to remain for some days at the ordinary temperature, when the yellow solution of the nitroso-derivative became quite colourless. The product was then cooled in a freezing mixture, acidified with sulphuric acid, and extracted with ether. On evaporating the ethereal solution, it deposited a colourless crystalline substance, which contained but traces of nitrogen, and therefore could not be nitrosoacetophenone. It is easily soluble in warm water, and on cooling crystallises in small thick prisms, which were collected, dried over sulphuric acid in a vacuum, and analysed, with the following results:—

- I. 0.1797 gram substance gave 0.0684 gram H_2O and 0.3962 gram CO_2 .
 II. 0.1247 gram substance gave 0.0477 gram H_2O and 0.2747 gram CO_2 .

	Found.		Theory. $C_9H_8O_4$.
	I.	II.	
C	60.13	60.08 per cent.	60.00 per cent.
H	4.22	4.25 „	4.44 „
O	35.65	35.67 „	35.55 „

The compound therefore appears to have the formula $C_9H_8O_4$. It crystallises from water in small prisms melting at 125° . It dissolves easily in alkalis, forming a colourless solution. On precipitating the neutral solution of the ammonium salt with silver nitrate, the silver salt was obtained as a voluminous white precipitate, which after being dried over sulphuric acid in a vacuum gave the following numbers on analysis:—

0.3050 gram substance gave 0.1147 gram Ag = 37.61 per cent.
 Theory, $C_9H_7O_4Ag$ = 37.63 „

I hope at some future time to be able to examine more thoroughly this curious reaction, and if possible to determine the constitution of the body $C_9H_8O_4$.

Dibenzoylacetic Acid.

In the preceding chapters, it has been shown that ethylic benzoylacetate is capable of forming derivatives in which the hydrogen atoms of the methylene group are displaced by alcoholic radicles such as ethyl, allyl, &c., in exactly the same way as ethylic acetoacetate. It was thought likely that very interesting results might be obtained if the acid chlorides such as benzoyl chloride were substituted for the iodides of the alcoholic radicles in the above reaction. If the sodium compound of ethylic benzoylacetate be heated with benzoyl chloride, the ethyl salt of dibenzoylacetic acid is formed according to the equation—

This ethereal salt on hydrolysis gives dibenzoylacetic acid,

When boiled with dilute acids, dibenzoylacetic acid is easily split up into acetophenone, benzoic acid, and carbonic anhydride, thus—

If boiled with water, a second reaction takes place at the same time, by which dibenzoylmethane is formed according to the equation—

In the preparation of ethylic dibenzoylacetate, it is not necessary to use the pure dry sodium compound of ethylic benzoylacetate and act on it with benzoyl chloride in ethereal solution, as was done in the first experiments, but we may proceed in the way usually employed in such syntheses, that is, by mixing ethylic benzoylacetate with sodic ethylate, and allowing benzoyl chloride to act directly on the product in the following way:—0.6 gram of sodium is dissolved in absolute alcohol, well cooled, and then mixed with 4 grams of ethylic benzoylacetate. 3 grams of benzoyl chloride are now added drop by drop, the whole being well cooled in a mixture of ice and salt. The reaction is very energetic, each drop of benzoyl chloride instantly producing a precipitate of chloride of sodium, and so much heat is developed that the alcohol will boil if a refrigerating mixture is not used. After all the benzoyl chloride has been added, the whole is warmed on a water-bath for about a quarter of an hour to insure the reaction being complete, and the greater part of the alcohol is distilled off; water is then added, and the product allowed to re-

main for some time, in order to insure the decomposition of any slight excess of benzoyl chloride. The watery liquid is next extracted with ether once or twice, the ethereal solution well shaken with carbonate of soda to remove benzoic acid, dried over potassium carbonate, and the ether distilled off. A thick dark brown oil remains behind. This was not further purified, although it is possible that by fractioning in a vacuum the ethylic dibenzoylacetate might be obtained in a pure state, as in the case of the ethyl- and allyl-benzoylacetates.

In order to obtain the free acid, the crude ethereal salt was hydrolysed by warming with an excess of alcoholic potash for about ten minutes on a water-bath. The mixture became dark coloured, and on adding water almost all of it dissolved, forming a dark brownish solution; this when acidified deposited the crude dibenzoylacetic acid as a thick oil, which became nearly solid on agitating for a short time. The product was collected, well washed with water, and dissolved in as little boiling alcohol (80 per cent.) as possible. On cooling, the acid crystallised out in colourless nodules, and was easily obtained pure and free from benzoic acid by repeated crystallisation. On analysis the following numbers were obtained:—

0.2257 gram substance gave 0.0925 gram H_2O and 0.5926 gram CO_2 .

	Found.	Calculated. $\text{C}_{16}\text{H}_{12}\text{O}_4$.
C	71.61 per cent.	71.64 per cent.
H	4.55 ,,	4.48 ,,
O	23.84 ,,	23.88 ,,

This substance was therefore dibenzoylacetic acid,
 $(\text{C}_6\text{H}_5\cdot\text{CO})_2\text{CH}\cdot\text{COOH}$.

The acid melts at 109° . When rapidly heated in small quantities, some of it distils undecomposed, but the greater part is split up into dibenzoylmethane and carbonic anhydride according to the equation—

Dibenzoylacetic acid is sparingly soluble in water and cold alcohol, but easily so in hot alcohol, benzene, and ether. The solution in alcohol gives a dirty red coloration on the addition of ferric chloride. The acid dissolves in concentrated sulphuric acid, producing a yellow solution, which, however, becomes colourless on warming. It dissolves slowly in solutions of ammonia, sodic hydroxide, and sodic carbonate, and is reprecipitated on the addition of an acid. In order to obtain a neutral solution of the ammonium salt, the pure acid was

dissolved in a slight excess of dilute ammonia, and then allowed to stand over sulphuric acid in a vacuum until the excess of ammonia had evaporated. The salt itself is very easily soluble in water; on boiling the solution, carbonic anhydride is given off, and the smell of acetophenone becomes noticeable. Several of the salts of dibenzoylacetic acid were prepared by precipitating the solution of the ammonium salt with various reagents. The *silver salt* is obtained on adding a solution of nitrate of silver as a white curdy precipitate, sparingly soluble in water. For analysis, the substance was dried at 80°.

0.1154 gram substance gave 0.0327 gram silver.

	Found.	Theory. (C ₆ H ₅ CO) ₂ CH.COOAg.
Ag	28.34 per cent.	28.72 per cent.

A solution of cupric sulphate precipitates the *copper salt* as a light yellowish-green mass, which appears to be somewhat soluble in hot water and alcohol. Prolonged boiling, however, decomposes the salt, cupric oxide being precipitated. This copper salt dissolves easily in ammonia, yielding a beautiful blue solution. The *barium salt* is soluble in water, and is prepared by shaking the finely powdered acid with baryta-water and a little alcohol for some time. After precipitating the excess of baryta by passing carbonic anhydride and filtering, a solution of the salt is obtained, which, however, is partly decomposed by evaporation. The *zinc salt* is also easily soluble in water. With a solution of the ammonium salt, acetate of lead gives a white curdy precipitate of the *lead salt*. With a solution of sulphate of nickel, the *nickel salt* is obtained as a light green precipitate soluble in excess of sulphate of nickel. Ferric chloride gives a brownish-red coloration with dilute solutions of the ammonium salt; with more concentrated solutions, however, the *ferric salt* is precipitated as a dirty reddish precipitate somewhat soluble in hot water. Ferrous sulphate gives the same reaction. Chloride of tin precipitates the *tin salt* as a heavy white mass sparingly soluble in water.

If dibenzoylacetic acid is mixed with alcoholic potash, a yellowish-green solution is formed which is decomposed by boiling, benzoic acid and a neutral body being formed. On distilling dibenzoylacetic acid with soda-lime, it is split up into benzene and an oily substance, which appears to be acetophenone.

In order to obtain pure ethylic dibenzoylacetate, the pure acid was dissolved in absolute alcohol, and hydrogen chloride passed through the solution until it was thoroughly saturated, the whole being kept well cooled during the operation. On adding water, an oil was precipitated, which, on distillation, came over almost entirely between

205—220° as a colourless oil smelling strongly of ethyl benzoate. The pure ether can easily be prepared, however, by decomposing the silver salt of the acid with ethylic iodide in ethereal solution. After filtering from the precipitated iodide of silver and evaporating on a water-bath, ethylic dibenzoylacetate remains behind as a thick colourless oil of a faint fruity odour; it does not solidify when cooled down to -10° .

Several experiments were next made in the hope of obtaining tribenzoylactic acid by treating ethylic dibenzoylacetate with sodic ethylate and benzoyl chloride as expressed in the equation—

In this way an almost colourless oil is obtained which, however, is unfortunately completely split up on hydrolysis, nothing but benzoic acid being formed.

As it appeared probable that ethylic tribenzoylacetate was really formed in the first place, an experiment was very carefully made with pure ethylic dibenzoylacetate, and the product freed from excess of benzoyl chloride and benzoic acid by shaking with dilute sodic carbonate was dried over carbonate of potash and analysed.

	Found.	Theory. ($\text{C}_6\text{H}_5.\text{CO}$) ₃ C.COOC ₂ H ₅ .	Theory. ($\text{C}_6\text{H}_5.\text{CO}$) ₂ CH.COOC ₂ H ₅ .
C	74.19 per cent.	75.00	72.97 per cent.
H	4.91 ,,	5.00	5.41 ,,
O	21.00 ,,	20.00	21.62 ,,

This ethereal salt is a very thick yellowish oil, which unfortunately could not be made to crystallise. On boiling it with dilute sulphuric acid, acetophenone and a solid acid, probably benzoic acid, are formed. It dissolves in alcoholic potash and is reprecipitated on adding a few drops of water, whereas ethylic dibenzoylacetate is only precipitated from its solution in alcoholic potash on the addition of a much larger quantity of water.

DECOMPOSITION-PRODUCTS OF DIBENZOYLACETIC ACID.

Dibenzoylmethane.

As dibenzoylactic acid contains two carbonyl-groups, it seemed probable that interesting results might be obtained by carefully examining its decomposition-products. The acid was therefore treated with several reagents; first of all with dilute sulphuric acid in the hope of simply splitting off carbonic anhydride, and thus obtaining dibenzoylmethane according to the equation—

The experiment was carried out in the following way:—A mixture of pure dibenzoylacetic acid with an excess of dilute sulphuric acid (1 : 2) was heated for about five hours in a flask connected with a reflux condenser; at the end of this a test-tube containing baryta-water was fixed, to serve as a rough indicator both of the quantity of carbonic anhydride and the rate at which it was given off.

The acid soon began to decompose and swam about in the liquid at first as a semi-solid mass, but later on in large oily drops, a considerable quantity of carbonic anhydride being evolved. At the end of the reaction, the contents of the flask, which smelt strongly of acetophenone, were subjected to distillation by steam; in this way a considerable quantity of a colourless oil passed over and was extracted by shaking with ether. On distilling off the ether and subsequent fractioning, nearly the whole of the residual oil passed over between 195—205°, and without doubt consisted of nearly pure acetophenone. In order to be certain, it was shaken with a solution of orthonitrobenzaldehyde in dilute sodic hydroxide, when a considerable quantity of indigo was precipitated after the mixture had been standing for some time.

On cooling, the residue in the flask deposited a quantity of glittering crystals which were collected and dried. They melted at 120° and showed all the properties of benzoic acid, with which they were no doubt identical.

Dibenzoylacetic acid is therefore decomposed by boiling with dilute sulphuric acid into benzoic acid, carbonic anhydride, and acetophenone according to the equation—

In repeating this reaction more carefully, it was noticed that if the boiling with sulphuric acid were stopped before all the dibenzoylacetic acid had been decomposed, a small quantity of a solid body, insoluble in sodic carbonate, could be isolated; when this is dissolved in alcohol and ferric chloride added, it gives a beautiful reddish-violet coloration. As, however, only very small quantities of this compound could be obtained by this method, several experiments were tried in order to improve the yield, and it was found that simple boiling with distilled water gave the desired result.

Pure dibenzoylacetic acid was boiled with water in a flask connected with a reflux condenser as long as carbonic anhydride continued to come off in any quantity (about 4—5 hours).

The acid melted slowly and sank to the bottom of the flask as a heavy, slightly brownish oil which on cooling partially solidified, the liquid becoming filled with needles of benzoic acid. A dilute solution of sodic carbonate was now added, and the whole well

shaken and allowed to stand for some time until all the benzoic acid had dissolved. After filtering and washing with water a small quantity of a semi-solid mass remained, smelling strongly of acetophenone; the latter can be roughly separated from the crystals by spreading them out on a porous plate or by pressing between blotting-paper. The crude product thus obtained was then dissolved in a little hot methyl alcohol from which it crystallised on cooling in beautiful flat plates; these are easily obtained pure by recrystallisation.

The analysis gave numbers agreeing with the formula —

0.1967 gram substance gave 0.0952 gram H_2O and 0.5772 gram CO_2 .

	Found.	Calculated. $\text{CH}_2(\text{CO}.\text{C}_6\text{H}_5)_2.$
C	80.03 per cent.	80.36 per cent.
H	5.37 ,,	5.36 ,,
O	13.60 ,,	14.28 ,,

This compound was therefore dibenzoylmethane or benzoylacetophenone. It melts at 81° and distils above 200° apparently without the least decomposition. It is easily soluble in ether, alcohol, and chloroform, the alcoholic solution, on the addition of a drop of ferric chloride, giving an intense reddish-violet coloration which resembles very closely that produced by benzoylactic acid itself. If the solution in hot methyl alcohol is cooled slowly, it crystallises most beautifully; it can, however, best be obtained in large crystals by allowing the ethereal solution to evaporate slowly. Professor Haushofer was kind enough to measure these crystals, and gave me the following description of them:—

Crystalline system rhombic:

$$a : b : c = ? : 1 : 1.38.$$

Small crystals with rhomboïdal base and extended in the direction of the makrodiagonal on which the surface $0\text{P}(c)$, $\infty\text{P}\infty(a)$, $\text{P}\infty(r)$ and an undetermined makrodome, d , were observed. The only surfaces fit for measurement were a , r , and in some crystals c . The

surface *d* is smooth, curved, and appears only on one-half of the crystals (with respect to the basal section). The surface *c* is also generally curved.

	Measured.	Calculated.
<i>r</i> : <i>r</i>	108° 18'	—
<i>c</i> : <i>r</i>	125° 54'	125° 51'
<i>a</i> : <i>r</i>	90°	90°

The compound is remarkable by the strong dispersion in its axes. The medial line is the vertical axis. The makropinacoid is the plane of the optical axis for the red, and the brachypinacoid for the blue. In the polariscope with white light, the surface *c* shows the interference figure of rhombic titanite acid (brookite).

Dibenzoylmethane is easily soluble in alkalis, particularly in alcoholic potash, and is reprecipitated unchanged on acidifying. It combines easily with phenylhydrazine, forming a solid substance which, however, was not further examined.

Tribenzoylmethane.

Dibenzoylmethane, $\text{CH}_2(\text{CO.C}_6\text{H}_5)_2$, contains a methylene-group associated with two carbonyl-groups, and for this reason is soluble in alkalis, forming metallic salts, the methylene-group in this body behaving in exactly the same way as the corresponding one in ethylic benzoylacetate, $\text{C}_6\text{H}_5.\text{CO.CH}_2.\text{COOC}_2\text{H}_5$. It appeared probable, therefore, that by further treatment with sodic ethylate and benzoyl chloride a tribenzoylmethane might be formed according to the equation—

This is in reality the case, as will be seen from the following experiment: 2 grams of pure dibenzoylmethane were mixed with a solution of 0.2 gram of sodium in absolute alcohol, and then as soon as all had completely dissolved 1.4 gram of benzoyl chloride was added drop by drop. Sodic chloride was immediately precipitated, the mixture becoming warm. After all the benzoyl chloride had been added, the product was heated on a water-bath for about ten minutes to ensure the reaction being complete; a quantity of water was then added, when a solid body separated; this was collected, well washed with water, and spread out on a porous plate to remove a small quantity of oil adhering to the crystals.

The compound was easily purified by recrystallisation from alcohol, and gave the following numbers on analysis:—

0.1849 gram substance gave 0.0864 gram H_2O and 0.5443 gram CO_2 .

	Found.	Theory. $\text{CH}(\text{CO}.\text{C}_6\text{H}_5)_3.$
C	80·28 per cent.	80·49
H	5·19 „	4·87
O	14·53 „	14·63

This substance, therefore, is tribenzoylmethane. On heating, it melts at 224—225°, and sublimes at a higher temperature almost without decomposition; in this respect it seems to be an extremely stable compound. Tribenzoylmethane is almost insoluble in cold alcohol, more easily soluble in hot, and crystallises from this solvent on cooling in small, almost microscopic, colourless needles. The hot alcoholic solution gives an orange coloration on adding a drop of ferric chloride. It is fairly easily soluble in benzene and carbon bisulphide, and crystallises in small needles on evaporating the solution. In chloroform and ether, on the contrary, it is sparingly soluble, and in light petroleum almost insoluble. It dissolves readily in alcoholic potash, and on adding water forms a colourless solution from which acids precipitate the original compound unchanged. On warming with concentrated sulphuric acid, it is coloured yellow. Nitric acid appears to entirely decompose it. Experiments were next made in the hope of obtaining tetrabenzoylmethane by the further action of sodic ethylate and benzoyl chloride on tribenzoylmethane, thus:—

By this means, a small quantity of a colourless body was obtained which, after being extracted several times with boiling alcohol, melted between 260—270°, and gave the following results on analysis:—

	Found.	Theory. $\text{C}(\text{C}_6\text{H}_5\text{CO})_4.$	Theory. $\text{CH}(\text{C}_6\text{H}_5\text{CO})_3.$
C	81·43 per cent.	80·58	80·49
H	5·15 „	4·63	4·87
O	13·42 „	14·80	14·63

As will be seen from the above, the analysis of such a substance does not show whether it is a tetra- or tri-benzoylmethane. The only fact which seems to prove that tetrabenzoylmethane had been formed is that the product is far more sparingly soluble in alcoholic potash than tribenzoylmethane. I hope at some future time to be able to continue the study of these interesting compounds, and if possible to improve the methods of preparing them.

Reduction of Ethylic Benzoylacetate.

Benzoylacetic acid being a ketonic acid, it was thought that it would be interesting to study the action of nascent hydrogen on it, in order, if possible, to obtain β -phenyllactic acid according to the equation—

In this reaction, it is better to use ethylic benzoylacetate than the free acid; the following method gives good results.

Ethylic benzoylacetate is dissolved in dilute sodic hydroxide solution, care being taken to avoid any large excess of alkali, and then 5 per cent. sodium amalgam is added in small portions at a time. The amalgam liquefies at first without evolution of hydrogen, the liquid becoming so warm that it is necessary to cool it continually. After about ten hours, hydrogen begins to be evolved, and the reaction is finished. The product is then filtered from a small amount of a resinous body (which will be described later on), the filtrate acidulated with dilute sulphuric acid, and extracted several times with ether. On distilling off the ether, an almost colourless oily acid remains, which does not solidify even after long standing in a vacuum over sulphuric acid. In order to purify it, the whole is converted into the barium salt by agitation with baryta-water, the excess of baryta removed by carbonic anhydride, and the precipitated barium carbonate filtered off. The colourless solution of the barium salt of the acid so obtained, is acidified with hydrochloric acid, shaken several times with ether, and the ethereal solution dried over chloride of calcium. On distilling off the ether, a very thick colourless oil is left; and this, on standing for some time, solidifies almost completely, especially after scratching the sides of the vessel containing it with a sharp glass rod. It may be purified by crystallising it once or twice from benzene, when it is obtained in beautiful colourless nodules consisting of fine needles. It melts at 93—94°, and gave the following numbers on analysis:—

0.2005 gram substance gave 0.1100 gram H_2O and 0.4760 gram CO_2 .

	Found.	Theory. $\text{C}_6\text{H}_5\text{CH}(\text{OH})\cdot\text{CH}_2\text{COOH}.$
C....	64.75 per cent.	65.06 per cent.
H....	6.09 ,,	6.03 ,,
O....	21.16 ,,	28.91 ,,

The substance was therefore β -phenyllactic acid, and was further identified by an analysis of the silver salt, which is easily obtained by precipitating a neutral solution of the ammonium salt with nitrate of silver, as a white curdy precipitate, somewhat soluble in water.

0.3360 gram substance gave 0.1330 gram $\text{Ag} = 39.58$ per cent.

Theory: $\text{C}_6\text{H}_5\text{CH}(\text{OH})\cdot\text{CH}_2\text{COOAg} = 39.56$,,

On heating this silver salt, it decomposes into silver carbonic anhydride and cinnamene, almost without charring. The acid itself, when

carefully heated, splits up almost quantitatively into water and cin-
namic acid, according to the equation—

This acid has all the properties of the β -phenyllactic acid prepared by Glaser (*Annalen*, **147**, 86) by the action of sodium amalgam on phenylchlorolactic acid, $\text{C}_6\text{H}_5.\text{CH}(\text{OH}).\text{CHCl}.\text{COOH}$, its formation from ethylic benzoylacetate being a proof that the hydroxyl group is really in the β -position. The same acid is also formed by boiling phenylbromopropionic acid, $\text{C}_6\text{H}_5.\text{CHBr}.\text{CH}_2.\text{COOH}$, with water (Fittig and Binder, *Annalen*, **195**, 138).

By the action of nascent hydrogen on ethylic benzoylacetate, there is always a certain amount of a resinous substance formed which separates out of the alkaline solution during the reduction, and can easily be freed from the sodic salt of the β -phenyllactic acid by filtration and washing with water. As in some cases a considerable amount of this compound was formed, it was thought that it might contain something definite, and was therefore carefully examined. The filter-papers were extracted with ether, and the ethereal solution filtered and evaporated; by this means a very thick dark-brown oil was left behind, which, after standing for several days, partly crystallised. The crystals were easily obtained colourless and free from oil, by repeated washings with small quantities of ether in which they are difficultly soluble. Last of all they were dissolved in a little hot alcohol, from which they crystallise on cooling in thick colourless prisms melting at 102° .

The analysis gave the following result:—

- I. 0.1665 gram substance gave 0.0768 gram H_2O and 0.4581 gram CO_2 .
- II. 0.2082 gram substance gave 0.0906 gram H_2O and 0.5720 gram CO_2 .

	Found.		Theory. ($\text{C}_5\text{H}_4\text{O}$) _n .
	I.	II.	
C	75.04	74.93 per cent.	75.00 per cent.
H	5.12	4.83 ,,	5.00 ,,
O	19.84	20.24 ,,	20.00 ,,

This substance therefore has the formula $(\text{C}_5\text{H}_4\text{O})_n$, most likely $\text{C}_{10}\text{H}_8\text{O}_2$.

When warmed with alcoholic potash, it yields an intense magenta-red solution; and on filtering and acidifying a colourless crystalline acid is precipitated. The alcoholic solution does not give any colour reaction with ferric chloride.

A small quantity of this body warmed with concentrated sulphuric acid dissolves, forming a pinkish solution with a slight greenish fluorescence. If, after standing for a short time, this solution be poured into water, a whitish amorphous substance separates; this forms an intense blue-green solution on the addition of an excess of sodic hydroxide. If the original substance, however, be more strongly heated with sulphuric acid, the pinkish colour first produced becomes browner, and at last of a deep olive-green. On pouring this olive-green solution into water, a bright yellowish liquid is produced, which, on the addition of sodic hydroxide, becomes of a beautiful purple. This reaction is extremely delicate, and is produced by mere traces of substance. This compound is isomeric with a substance which was obtained by the action of sodium on acetate of phenyl, a reaction which W. R. Hodgkinson and I studied some time ago (*Trans.*, 1880, 487). Curiously enough the latter also gives the same characteristic reaction when warmed with potash; the red colour is destroyed, however, on diluting with water, which is not the case with the body described above.

Action of Phosphorous Pentachloride on Ethylic Benzoylacetate.

Geuther (*Zeitschr. f. Chem.*, 1871, 237), who was the first to study the action of pentachloride of phosphorus on ethylic acetoacetate, found that when it was treated with an excess of the former it was resolved into the chlorides of two isomeric chlorcrotonic acids, namely, β -chlor- α -crotonic acid, $\text{CH}_3\text{CCl}:\text{CH}.\text{COOH}$, and the β -chloro- β -crotonic acid, $\text{CH}_2:\text{CCl}.\text{CH}_2.\text{COOH}$.

On decomposing these chlorides with water, and distilling with steam, the β -chloro- β -crotonic acid distils over first, and then the β -chlor- α -crotonic acid. As the methyl group of the ethylic acetoacetate must have taken part in the formation of β -chloro- β -crotonic acid, supposing the formula $\text{CH}_2:\text{CCl}.\text{CH}_2.\text{COOH}$ to be correct, it appeared interesting to repeat these experiments with ethylic benzoylacetate, in which the presence of the phenyl group would shut out the possibility of the formation of any acid analogous in constitution to β -chloro- β -crotonic acid.

In order to test this, 10 grams of ethylic benzoylacetate was dissolved in 25 grams of oxychloride of phosphorus, and 25 grams of phosphorous pentachloride slowly added. As the reaction appeared to take place very slowly at ordinary temperatures, the mixture becoming only slightly warm, the whole was heated for about half an hour on a water-bath, when the pentachloride slowly disappeared, hydrogen chloride being given off. As soon as the reaction was over, the oxychloride of phosphorus was distilled off on a water-bath in a

vacuum, the latter portions carrying over a small quantity of a crystalline substance which sublimed into the condenser in yellow needles; these, however, were not further examined. The residue, consisting of a dark-brown oil, was poured into ice-water and allowed to remain for some time, in order that acid chlorides and any excess of pentachloride of phosphorus might be entirely decomposed. An excess of sodic carbonate was then added, and the whole gently warmed with animal charcoal on a water-bath for about fifteen minutes, and filtered. On acidifying the filtrate, which was nearly colourless, it deposited a crystalline acid; this was collected, well washed, and recrystallised twice from alcohol. It was thus obtained perfectly pure in beautiful glittering plates, which, on analysis, gave the following result:—

0.1798 gram substance gave 0.0665 gram H_2O and 0.3901 gram CO_2
 0.2424 „ „ 0.3080 $AgCl$.

	Found.	Theory. $C_9H_7O_2Cl$.
C	59.17 per cent.	59.18 per cent.
H	4.10 „	3.84 „
Cl	19.47 „	19.45 „
O	17.26 „	17.53 „

The compound was therefore chlorocinnamic acid, produced according to the equations—

By this reaction, therefore, β -chlorocinnamic acid should be obtained. There are two monochlorocinnamic acids known, the α -monochlorocinnamic acid, $C_6H_5.CH:CCl.COOH$, and the β -monochlorocinnamic acid, $C_6H_5.CCl:CH.COOH$. These were obtained by Jutz (*Ber.*, **15**, 788), in a way exactly similar to that employed by Glaser (*Annalen*, **143**, 330), in the preparation of the monobromocinnamic acids, namely, by heating phenyldichloropropionic acid with potash:—

He separated these acids by means of the potash salts, the salt of

the α -acid being sparingly soluble in water, whereas the salt of the β -acid is easily soluble. The α -chlorocinnamic acid, crystallised from water, melts at $137-138^\circ$, crystallised from light petroleum at 142° . β -Chlorocinnamic acid melts at 114° . α -Chlorocinnamic acid is also formed by heating phenylchlorolactic acid with water at $120-200^\circ$:—

This is a proof that the chlorine is in the α -position, there being no doubt as to the constitution of phenylchlorolactic acid. A further proof of the constitution of α -chlorocinnamic acid is its formation by the action of acetic anhydride on a mixture of benzaldehyde with sodic monochloracetate, according to the equation—

(Plöchl, *Ber.*, **15**, 1945).

The chlorocinnamic acid obtained from ethylic benzoylacetate by the action of pentachloride of phosphorus in the way just described, melts at 142° , and possesses, strangely enough, all the properties of α -chlorocinnamic acid, with which it is no doubt identical, although, according to the equation given above, β -chlorocinnamic acid should be produced.

The formation of α -chlorocinnamic acid from ethylic benzoylacetate in this way is difficult to explain; one is forced to come to the conclusion that the β -acid is first formed, and afterwards, under the influence of such powerful reagents as pentachloride and oxychloride of phosphorus, that a molecular change takes place, whereby the β -acid is transformed into the α -acid. In the case of the monobromocinnamic acids, the β -acid can with the greatest ease be transformed into the α -acid by distillation, or by heating with hydriodic acid, the change being almost quantitative. Still stranger is the fact that the β -monobromocinnamic acid on etherification is converted quantitatively into the ethyl salt of α -monobromocinnamic acid. This mobility of the bromine-atom makes it appear possible that these compounds are merely physical isomerides, and not chemical isomerides in the true sense of the word.

Condensation of Ethylic Benzoylacetate with Benzaldehyde.

The hydrogen-atoms of the methylene group in ethylic acetoacetate are very easily substituted by condensation with aldehydes, according to the equation (Claisen, *Annalen*, **218**, 170)—

This condensation is best brought about by mixing the ethylic acetoacetate with the calculated amount of the aldehyde, and then after cooling in a freezing mixture, saturating the whole with hydrogen chloride. After standing for about two days, the reaction is complete, the resulting product, *e.g.*, in the case of the condensation of ethylic acetoacetate with benzaldehyde, consisting of a mixture of two isomeric ethylic acetylbenzylchloracetates—

which are easily separated by crystallisation from light petroleum. Both these compounds are decomposed by distillation, yielding hydrogen chloride and ethylic acetylbenzalacetate—

Claisen explains this condensation by supposing that the aldehyde is first converted by the hydrochloric acid into an unstable chlorhydrol, $\text{R}.\text{CH}(\text{OH})\text{Cl}$, which then acts on the ethylic acetoacetate in the following way:—

On substituting benzoylacetate for ethylic acetoacetate, it was found that condensation with aldehydes took place in precisely the same way. As it appeared interesting to prove the analogy between ethylic benzoylacetate and acetoacetate in this respect also, the condensation of the former with benzaldehyde was further studied.

10 grams of ethylic benzoylacetate were mixed with 5 grams of benzaldehyde, and the whole, after being cooled below 0° in a freezing mixture, was completely saturated with hydrogen chloride. The product soon became very thick and milky, from the formation of minute globules of water, which, after standing for 24 hours at the ordinary temperature, settled out in large drops on the side of the vessel.

The dark brown oily product was dissolved in ether, well washed, first with water and then with sodic carbonate solution, to remove the excess of hydrochloric acid, and finally dried over potassic carbonate. After filtering and distilling off the ether, a dark brownish very thick oil remained; this was distilled as rapidly as possible under diminished pressure (200 mm.), only a small residue being left. The distillate, which was nearly colourless, was distilled again, under the same pressure, the first portions, consisting of acetophenone and unchanged benzaldehyde, being rejected; afterwards a thick oil came over, which rapidly solidified on standing.

The latter was dissolved in hot methyl alcohol, from which on cooling it crystallised in beautiful colourless needles, easily obtained pure by recrystallisation.

The analysis of the crystals, dried at 70—80°, gave the following numbers:—

- I. 0.2243 gram of substance gave 0.1195 gram H_2O and 0.6321 gram CO_2 .
 II. 0.2022 gram of substance gave 0.1040 gram H_2O and 0.5665 gram CO_2 .

	Found.		Theory.
	I.	II.	$C_6H_5.CO.C \begin{smallmatrix} \swarrow CH.C_6H_5 \\ \searrow COOC_2H_5 \end{smallmatrix}$
C	76.86	76.83 per cent.	77.14 per cent.
H	5.91	5.74 ,,	5.72 ,,
O	17.23	17.43 ,,	17.14 ,,

The compound is therefore ethylic benzalbenzoylacetate. Ethylic benzalbenzoylacetate crystallises from methyl alcohol in long colourless glittering prisms, which melt at 98—99°. It is pretty easily soluble in hot methyl alcohol, sparingly so in cold. Like ethylic acetylbenzalacetate, it crystallises very readily. It separates from a mixture of benzene and light petroleum in flat plates, which polarise light splendidly. It crystallises best, however, from ether. If the ethereal solution is allowed to evaporate slowly, the sides and bottom of the vessel containing it become covered with large transparent glittering prisms, which do not lose their lustre on drying. Professor Haushofer, who kindly measured some of the crystals, gave me the following description of them:—

Crystalline system monoclinic:

$$a : b : c = 1.2730 : 1 : 0.7461. \quad \beta = 86^\circ 36'.$$

Pale yellow lustrous crystals, forming the combinations $\infty P\infty(a)$, $\infty P(p)$, $-P\infty(r)$, $P\infty(s)$, extended in the direction of the ortho-

diagonal, often also tabular on the surface a . The surfaces of this zone are smooth, but as a rule indented, and the measurements are therefore somewhat irregular.

	Measured.	Calculated.
$p : p = 103^{\circ} 36'$		—
$r : p = 109 37$		—
$s : r = 119 20$		—
$r : a = 122 57$		$122^{\circ} 53'$
$p : a = 128 30$		128 12
$s : a = 117 53$		117 47
$s : p = 106 40$		106 45

Ethyl benzalbenzoylacetate dissolves in sulphuric acid, producing a yellow solution, which, however, becomes colourless again on standing or gently warming. The solution of this body in chloroform is only very slowly attacked by bromine.

Several saponification experiments were next made, in the hope of obtaining benzylideneacetophenone, according to the equation—

but without result. When ethyl benzalbenzoylacetate was heated with dilute hydrochloric acid in a sealed tube at 160° for seven hours, it was decomposed in part, producing a yellow oil. On opening the tube, large quantities of carbonic anhydride escaped, and on fractioning the product a considerable amount was obtained boiling below 210° , and consisting of a mixture of benzaldehyde and acetophenone. The thermometer was then removed, and the residue distilled in a vacuum, when a thick oil came over, which solidified on cooling. After crystallisation from methyl alcohol, it melted at 98° , and showed all the properties of ethyl benzalbenzoylacetate. Negative results were also obtained on boiling it with potash, only small quantities of benzoic acid being produced.

Claisen (*Annalen*, **218**, 173) obtained similar results on trying to obtain ethylideneacetone and crotonic acid by saponifying ethyl acetylethylideneacetate, $\text{CH}_3\text{.CH} \begin{smallmatrix} \text{CH}_3\text{.CH} \\ \text{CH}_3\text{.CO} \end{smallmatrix} \gg \text{C.COOC}_2\text{H}_5$, with potash, and attributes this to the fact of the latter class of bodies being so easily decomposed into their components, and thus giving only aldehyde and the decomposition-products of ethyl acetoacetate, respectively ethyl benzoylacetate on hydrolysis. Another method employed by Claisen to effect the condensation of aldehydes with ethyl acetoacetate was by heating a mixture of the two bodies in a sealed tube with acetic anhydride. In order to see whether this also took place in the case of ethyl benzoylacetate, 10 grams of the latter, 5 grams of benzaldehyde, and an excess of acetic anhydride, were heated together in a sealed tube at $180\text{--}200^{\circ}$ for six hours. On opening the

tube a large quantity of carbonic anhydride escaped. The product, which was a dark brown oil, was then directly fractioned. Below 100° , a small quantity of a limpid oil came over, which, after washing and refractioning, distilled almost entirely between 70° and 80° as a light oil, smelling strongly of ethylic acetate. After the excess of acetic anhydride and acetic acid had distilled over, the thermometer rose rapidly to 180° , and between that and 210° a considerable quantity of a mixture of benzaldehyde and acetophenone came over. The residue was then distilled under diminished pressure, when the latter portions, which were collected separately, partially solidified on cooling. The crystals were first roughly freed from oily matter, by spreading them out on a porous plate, and then purified by crystallisation, once from methyl alcohol and once from ether.

The analysis gave the following numbers:—

0.1863 gram substance gave 0.0976 gram H_2O and 0.5254 gram CO_2 .

	Found.	Theory.
		$\begin{array}{l} \text{C}_6\text{H}_5\cdot\text{CO} \\ \text{C}_6\text{H}_5\cdot\text{CH} \end{array} \begin{array}{l} \text{C} \\ \text{C} \end{array} \text{COOC}_2\text{H}_5$
C	76.92 per cent.	77.14 per cent.
H	5.82 „	5.72 „
O	17.26 „	17.14 „

The crystals melted at 98° , and the body was therefore ethylic benzalbenzoylacetate. The yield by this method was not nearly so good as by the one previously described. It is possible that the temperature employed (180 — 200°) was too high, and that some of the product was again resolved into its components, the ethylic benzoylacetate being further decomposed into acetophenone and carbonic anhydride.