XVIII.—*Condensation of Benzile with Ethylic Malonate.*

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By the condensing action of sodium ethoxide on a mixture of benzile and ethylic malonate we have obtained two compounds: (1) ethylic

hydrogen benzoïnylmalonate, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CO} \end{array} \begin{array}{l} \text{COOC}_2\text{H}_5 \\ \text{COOH} \end{array}$, and (2) desylenemalonic acid, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{C}(\text{COOH})_2 \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CO} \end{array}$ *

When the former compound is warmed with glacial acetic acid, it parts with water, yielding the monethylic salt of the latter.

By boiling desylenemalonic acid with fuming hydriodic acid, it is transformed into a mixture of Victor Meyer and Oelker's desylacetic acid and Klingemann's diphenylcrotonolactone, carbon dioxide being eliminated in the process:

Diphenylcrotonolactone.

Diphenylcrotonolactone was obtained by Klingemann (*Annalen*, **269**, 134) by the dehydrating action of heat on desylacetic acid. In the present case, it might be formed either directly from desylenemalonic acid, or, indirectly, by the dehydration of desylacetic acid, the latter being the primary product of the interaction; but we did not further investigate this point.

When heated above its melting point, desylenemalonic acid parts with carbon dioxide, yielding desyleneacetic (β -benzoyleinnamic) acid,

* The name "desylene," denoting the dyad group, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C} \cdot \text{C}_6\text{H}_5$, is formed on the analogy of Victor Meyer's "desyl," $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH} \cdot \text{C}_6\text{H}_5$.

$$\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{C}\cdot\text{CH}\cdot\text{COOH} \\ | \\ \text{C}_6\text{H}_5\cdot\text{CO} \end{array}$$
 This substance was obtained in two forms, melting respectively at 150° and 169° , both of which gave, on analysis, figures agreeing with the foregoing formula; but we incline to regard this difference as due to dimorphism rather than to stereoisomerism, as the former modification, on keeping, spontaneously changed its melting point and, after a lapse of two or three weeks, melted, like the latter, at 169° . Another acid, melting at 261° , was also isolated from the product of the action of heat on desylene-malonic acid, but in quantity too small for analysis.

EXPERIMENTAL PART.

Ethylic Hydrogen Benzoïnylmalonate.—Fifty grams of benzile, powdered as finely as possible, and 38 grams of ethylic malonate were introduced into a flask, after which a solution of sodium ethoxide, obtained by dissolving 5.5 grams of sodium in 65 grams of absolute alcohol,* was added, and the flask corked and shaken. The mixture, which turned reddish-brown on the addition of the ethoxide, became gradually thicker, until, after about an hour and a half, it formed a semi-solid mass. It was then allowed to stand for two days, during which time the colour gradually changed to a yellowish-brown. The product was shaken with ether and water simultaneously, in the hope that the ether would dissolve benzile and non-acid substances, whilst acids would be found in the aqueous solution in the form of their sodium salts; but after the mass was completely disintegrated, it was found that there was a white crystalline powder which dissolved neither in the water nor in the ether, and prevented the separation of the two liquids. The crystalline powder, which proved to be ethylic sodium benzoïnylmalonate, was separated by filtration and washed, first with cold water and then with ether.

After the removal of the solid substance, the ethereal and aqueous solutions were separated. The former yielded on evaporation nothing but benzile, half the quantity taken being in this way recovered. The aqueous solution was acidified with dilute sulphuric acid, and the copious precipitate of organic acid extracted with ether. On shaking this ethereal solution with sodium carbonate, a fresh precipitate of ethylic sodium benzoïnylmalonate was produced, the quantity of which increased on standing. This precipitate was separated by filtration, treated as above, and added to the portion already obtained. We describe later on the treatment of the aqueous sodium carbonate solution, which we will distinguish as A.

* If this proportion of alcohol is much exceeded, the benzile is converted mainly into ethylic benzoate and benzaldehyde.

The sparingly soluble sodium salt, of which the total yield was about 70 grams, was found to dissolve readily in hot water; but it speedily decomposed in the hot solution, benzile separating. If the solution was heated on the water bath until no more benzile separated, the filtered liquid gave no precipitate on adding sulphuric acid. It doubtless contained malonic acid produced by hydrolysis; but we did not examine it further.

In order to isolate the acid from the sodium salt, the latter was suspended in water, and, after adding dilute sulphuric acid, the mixture was shaken with ether until all the solid was dissolved. After separating the ethereal solution and distilling off the ether at a low temperature, a gummy mass was obtained which was dissolved in ethylic acetate, and light petroleum added. The substance at first separated as an oil, but, by rubbing it with a glass rod, crystallisation was induced. It formed large, lustrous, apparently rectangular prisms melting at 134°. Analysis gave figures agreeing with the formula of

0.1523 gave 0.3727 CO₂ and 0.0743 H₂O. C = 66.74; H = 5.42.

C₁₉H₁₈O₆ requires C = 66.67; H = 5.26 per cent.

The *ethylic sodium salt* was then regenerated from the acid ethylic salt by shaking an ethereal solution of the latter with an aqueous solution of sodium carbonate. It separated, as before, in the form of a sparingly soluble, crystalline powder, and was purified by washing it, first with cold water and then with ether. When heated at 100° it turned yellow. It was therefore dried for analysis at 40–55°.

0.5983 gave 0.1177 Na₂SO₄. Na = 6.37.

C₁₉H₁₇O₆Na requires Na = 6.32 per cent.

Ethylic Hydrogen Desylenemalonate.—In our first attempt to prepare the acid ethylic salt from the sparingly soluble sodium salt, we dissolved the latter in hot glacial acetic acid. On diluting the solution with water, a substance was deposited in rosettes of long, clear needles. It was purified by dissolving it in a small quantity of ethylic acetate and adding a large excess of light petroleum; from this solution it separated in rosettes of slender, lustrous prisms melting, not very sharply, at 124°. The substance was an acid, and dissolved readily in sodium carbonate; but, that it was not the acid corresponding with the sodium salt from which it had been obtained was evident, inasmuch as its sodium salt was readily soluble, and, when the solution was digested on the water bath, gave no separation of benzile.

Analysis showed that it had been formed from ethylic hydrogen

benzoïnylmalonate by the abstraction of the elements of a molecule of water.

0·1401 gave 0·3611 CO₂ and 0·0642 H₂O. C = 70·29; H = 5·09.

0·1621 „ 0·4177 CO₂ „ 0·0749 H₂O. C = 70·28; H = 5·13.

C₁₉H₁₆O₅ requires C = 70·37; H = 4·94 per cent.

This compound is *ethylic hydrogen desylenemalonate*,

When warmed on the water bath with sodium hydroxide, it is hydrolysed, and, on acidifying the solution, desylenemalonic acid (see following section) is precipitated.

Desylenemalonic acid.—The filtrate, A, was digested on the water bath until benzile, produced by the hydrolysis of ethylic sodium benzoïnylmalonate, ceased to separate. The solution, filtered from the benzile and acidified with sulphuric acid, gave a precipitate, which, after purifying by a process to be described later on, gave figures agreeing with those required for desylenemalonic acid.

If, however, the other compounds above described are not required, the following method gives the best yield of desylenemalonic acid. The product of the action of sodium ethoxide on a mixture of benzile and ethylic malonate, employing the proportions above given, is shaken with a mixture of ether and very dilute sulphuric acid. In this way, all the organic acids are liberated, and, along with unaltered benzile, dissolve in the ether. The ethereal solution is separated, the ether removed by distillation, and the residue dissolved in excess of glacial acetic acid. The greater part of the acetic acid is then distilled off over a free flame, any ethylic hydrogen benzoïnylmalonate being thus converted into ethylic hydrogen desylenemalonate, and water is added to the remainder. The precipitated organic substance is again dissolved in ether, and the solution shaken with an aqueous solution of sodium carbonate, to remove acids, the separated sodium carbonate solution being extracted with a fresh quantity of ether, to get rid of the last traces of benzile. The aqueous solution then contains sodium desylenemalonate and ethylic sodium desylenemalonate. In order to hydrolyse the latter, excess of sodium hydroxide is added, and the solution is digested on the water bath for some hours. It is then filtered from any resin that may have separated, after which, the desylenemalonic acid is precipitated with dilute sulphuric acid. The desylenemalonic acid is purified by dissolving it in the smallest possible quantity of ethylic acetate and adding excess of benzene, when it separates very slowly in slender, felted needles, apparently containing benzene of crystallisation.

The yield from 50 grams of benzile, 38 grams of ethylic malonate, 5.5 grams of sodium, and 65 grams of alcohol was only 24 grams; but, as in the experiment already described, about half the benzile was recovered unchanged.

For most purposes, the desylenemalonic acid, thus obtained, is sufficiently pure, but it has a pale brown colour, and the melting point is not sharp. For analysis, it was purified by converting it into its sparingly soluble calcium salt, decolorising the solution by boiling it with animal charcoal, and recrystallising the salt. The acid was obtained from this salt by shaking it with a mixture of dilute hydrochloric acid and ether. The acid, left on evaporating the ether, was finally purified by recrystallisation from a mixture of ethylic acetate and benzene.

Desylenemalonic acid forms colourless, slender, felted needles, which become opaque on drying. It melts at 130° . When heated above its melting point, it evolves gas and becomes dark coloured. For analysis, it was dried at 100° .

The analytical figures agreed with the formula $C_{17}H_{12}O_5$.

0.1279 gave 0.3240 CO_2 and 0.0480 H_2O . C = 69.09; H = 4.17.

0.2040 „ 0.5155 CO_2 „ 0.0753 H_2O . C = 68.91; H = 4.10.

$C_{17}H_{12}O_5$ requires C = 68.92; H = 4.05 per cent.

It has the constitution
$$\begin{array}{c} C_6H_5 \cdot C \cdot C(COOH)_2 \\ | \\ C_6H_5 \cdot CO \end{array}$$

The *silver salt*,* which was prepared by precipitating the ammonium salt with silver nitrate, is very sparingly soluble in cold water, but dissolves in boiling water almost without decomposition, and is deposited in needles from the cooled solution. For analysis, it was dried at 100° .

0.1288 gave 0.0545 silver. Ag = 42.31.

$C_{17}H_{10}O_5Ag_2$ requires Ag = 42.35 per cent.

Action of Hydriodic acid on Desylenemalonic acid.—Desylenemalonic acid was boiled with excess of fuming hydriodic acid ($d\ 1.96$) for five minutes in a flask over a bare flame, shaking the mixture during the process. The substance fused, and iodine was given off. Water was then added, and the dark-coloured, oily, organic substance which separated was washed with water, dissolved in ether, and the ethereal solution freed from iodine by shaking it with a dilute aqueous solution of sulphurous acid. The ethereal solution was washed with water and then shaken with a solution of sodium carbonate, which extracted from it an organic acid, whilst a non-acid substance remained in the ether, and was obtained as a crystalline residue on evaporation. This

* Prepared and analysed by Mr. G. Druce Lander, B.Sc.

non-acid substance is not very soluble in ether, and, unless a sufficiency of ether is employed, is apt to separate before the acid has been extracted.

The sodium carbonate solution gave, on acidifying with dilute sulphuric acid, a precipitate of an organic acid, which was extracted with ether, and, after expelling the ether, recrystallised from hot benzene. It formed lustrous crystals, of octahedral habit, melting at 160° . Analysis of the substance, dried at 100° , gave figures agreeing with the formula $C_{16}H_{14}O_3$.*

0.1315 gave 0.3647 CO_2 and 0.0659 H_2O . $C = 75.64$; $H = 5.57$.
 $C_{16}H_{14}O_3$ requires $C = 75.59$; $H = 5.51$ per cent.

This is the formula of *desylacetic acid*, $\begin{array}{c} C_6H_5 \cdot CH \cdot CH_2 \cdot COOH \\ | \\ C_6H_5 \cdot CO \end{array}$, and the melting point (160°) very nearly agrees with that found by Knoevenagel (*Ber.*, 1888, **21**, 1350) for this substance (162°). The substance was therefore compared with a specimen of desylacetic acid prepared by Knoevenagel's method (from sodio-deoxybenzoïn and ethylic iodacetate, afterwards hydrolysing the ethereal salt thus obtained), and was found to be indistinguishable from it, except that this specimen, which had been more frequently recrystallised, melted one degree higher than our acid.

The non-acid substance above referred to, which remained after expelling the ether, was recrystallised from hot benzene. It was deposited in tufts of slender needles, melting constantly at 151.5° . Analysis of the substance, dried at 100° , gave figures agreeing with the formula $C_{16}H_{12}O_2$.

0.1450 gave 0.4322 CO_2 and 0.0682 H_2O . $C = 81.29$; $H = 5.23$.
 $C_{16}H_{12}O_2$ requires $C = 81.35$; $H = 5.09$ per cent.

This is the formula of *diphenylcrotonolactone*, $\begin{array}{c} C_6H_5 \cdot C - CH_2 \\ || \quad | \\ C_6H_5 \cdot C \quad CO \\ \quad \quad \quad \backslash \\ \quad \quad \quad O \end{array}$, a com-

pound formed from desylacetic acid by abstraction of water, and the melting point agrees exactly with that given by Klingemann (*loc. cit.*)

Desyleneacetic (β -Benzoylcinnamic) acid.—As a dicarboxylic acid in

* The substances used for this and the next following analysis were, we should mention, obtained by the action of hydriodic acid on the monethylic salt of desylenemalonic acid. We happened to have a quantity of this compound, and used it for the interaction without previously converting it into the acid. It is hydrolysed by the hydriodic acid, and consequently gives the same products as desylenemalonic acid itself, as we convinced ourselves by a careful comparison of the substances obtained in the two cases.

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which both carboxyl groups were attached to the same carbon atom, it was probable that desylenemalonic acid would part with carbon dioxide when heated, yielding a monobasic acid. The evolution of gas already referred to, observed when the substance was heated above its melting point, was doubtless to be interpreted in this sense.

In order to obtain the monobasic acid, we at first tried the plan of distilling desylenemalonic acid under reduced pressure. From the distillate we had no difficulty in isolating an acid of the expected composition; but the yield was only one-fortieth of the weight of desylenemalonic acid taken. However, by merely heating the desylenemalonic acid until carbon dioxide ceased to be evolved, a better yield, although still a very poor one, was obtained.

The desylenemalonic acid was introduced into a tubulated distilling flask, which was exhausted during the whole operation by means of a filter-pump, in order to prevent aerial oxidation. The flask was heated in a glycerol bath at 180—200° for two hours, at the end of which time the evolution of carbon dioxide had practically ceased. The dark violet-coloured mass was dissolved in ether, and the ethereal solution shaken with aqueous sodium carbonate; the carbonate solution was acidified with dilute sulphuric acid, and the precipitated acid, after extraction with ether, purified by recrystallisation from benzene. It was found, however, that the crystals, which were large and well formed, obstinately retained a brown colour; but, by digesting them on the water bath with a small quantity of benzene, they disintegrated, forming a white powder from which the hot benzene, containing the greater part of the colouring matter, could be poured off; on dissolving this powder in more hot benzene, a solution was obtained which deposited colourless crystals, melting constantly at 169°. The yield from 25 grams of desylenemalonic acid was only 4 grams.

Analysis of a specimen prepared by the distillation method, having a faint brownish tinge, and melting at 168°,* gave figures agreeing with the formula $C_{16}H_{12}O_3$.

0.1008 gave 0.2813 CO_2 and 0.0435 H_2O . $C = 76.11$; $H = 4.79$.

$C_{16}H_{12}O_3$ requires $C = 76.19$; $H = 4.76$ per cent.

The compound is, therefore, *desyleneacetic* (β -benzoylcinnamic) acid,
 $C_6H_5 \cdot \overset{\cdot}{C} : CH \cdot COOH$
 $C_6H_5 \cdot \overset{\cdot}{CO}$

A compound of this formula ought to be capable of existing in two stereoisomeric forms, and we at one time thought we had actually obtained the two isomerides. A specimen of the substance, prepared by the distillation method, gave, on recrystallisation

* This specimen was prepared and analysed before we had hit upon the foregoing method of purifying the substance.

from benzene, two distinct forms, which could without difficulty be mechanically separated; clear, brownish crystals, grouped in rosettes, melting at 168° (the specimen used for the foregoing analysis); and colourless, more or less opaque, single crystals, melting at 150° . The latter gave, on analysis, $C = 75.95$, $H = 4.96$, showing that they had the same composition as the others. Some weeks later, the melting point of these crystals was redetermined, and was found to have risen to 169° , the melting point of the form already described. We must, therefore, regard this supposed isomeride (which we obtained only once) as an unstable crystalline form of the substance melting at 169° . Neither of the forms contained benzene of crystallisation.

The *silver salt** was obtained as a white precipitate, by adding silver nitrate to a solution of the ammonium salt. It is not decomposed by boiling with water, in which it is almost insoluble.

0.2194 gave 0.0658 silver. $Ag = 29.99$.

$C_{16}H_{11}O_3Ag$ requires $Ag = 30.08$ per cent.

In the preparation of desylacetic acid by merely heating desylene-malonic acid without distilling it, a small quantity of a white crystalline acid melting at 261° was obtained. It formed a sparingly soluble sodium salt. The quantity was insufficient for further examination.

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