XXX.—*Contributions to the Knowledge of the β -Ketonic Acids.* Part III.

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THE compounds formed by the action of ethylic chlorofumarate and ethylic α -chlorocrotonate on ethereal salts of β -ketonic acids have hitherto been regarded as hydrogenised furfuran derivatives (Trans., 1896, 69, 530, 1383), and this view seemed to agree well with their behaviour. Further study, however, has led to results which modify this view and tend to show that these substances must be regarded as ketonic compounds. It was stated (*loc. cit.*) that the ethereal salt formed from the sodium deriva-

tive of ethylic acetoacetate and ethylic chlorofumarate was to be represented by the formula I, and that this expression agreed with the result

of the refractometric behaviour of the compound. An error, however, was made in the calculation of the molecular refraction; the number 71.94, there given, corresponds with that required for ethylic acetoacetonate, II, which agrees with the refractometric constant found (*loc. cit.*, p. 532) 72.23, whilst formula I requires the value 70.19.

It was shown that, in using ethylic chloromaleate, the same compound was formed as in the interaction of the sodium derivative of ethylic acetoacetate with ethylic chlorofumarate. This fact, which was brought forward as a further argument in favour of the view there expressed, must be explained by assuming a molecular transformation. On the other hand, formula II admits of as ready an explanation of its transformations as does formula I, and is, moreover, in full agreement with the behaviour of ethylic chlorofumarate and ethylic α -chlorocrotonate towards the sodium derivatives of other β -ketonic acids.

Corresponding formulæ have to be attributed to the ethereal salts formed from ethylic benzoylacetate and ethylic chlorofumarate, and also to that obtained by the action of ethylic acetoacetate on ethylic α -chlorocrotonate, namely,

Ethylic aceto- β -butylenedicarboxylate.

The formation of acetonylmalic acid* and of acetophenylmalic acid

* Dr. A. Hutchinson has been kind enough to make the following crystallographic measurements of acetonylmalic acid.

Crystalline system :—Monoclinic (Holoedric).

$$a : b : c = 0.719 : 1 : 0.478.$$

$$\beta = 53^\circ 8'.$$

Forms observed :— $c\{001\}$, $p\{110\}$, $o\{\bar{1}11\}$.

The following measurements were made.

	Angle.	Mean value.	Calculated.
pp'	$= 110 : \bar{1}10$	$120^\circ 10'$	—
pc	$= 110 : 001$	58 40	—
oc	$= 111 : 001$	47 30	—
oo'''	$= \bar{1}11 : \bar{1}\bar{1}1$	50 50	$51^\circ 0'$

from ethylic acetoacnitrate and from ethylic benzoylaconitate respectively is brought about by the elimination of carbon dioxide, accompanied by the addition of 1 molecule of water, and their formulæ do not, therefore, differ from those given before; they are expressed by the symbol

The constitution of the compounds formed from ethylic acetoacnitrate, and from ethylic benzoylaconitate, under the influence of ammonia, needs no modification, notwithstanding this change of view. But the product resulting from the action of ammonia on ethylic aceto- β -butylenedicarboxylate (*loc. cit.*, p. 1393) has to be regarded as a monamide of the formula

Ethylic chlorofumarate, as shown before (*loc. cit.*, p. 1386), reacts with the sodium derivative of ethylic acetomethylacetate with elimination of ethylic acetate and formation of a compound which, in the light of the former view, was regarded as ethylic furfurandicarboxylate,

This constitution, however, does not agree with the result of further study, which led to the conclusion that the reaction takes place as indicated by the following equation:

The crystals were obtained from aqueous solution, and a large number from three different preparations examined.

All the crystals are of well-marked rhombohedral habit. This is due to the equal development of the faces *c* and *p*, and to the near equality of the angles $001:110 = 58^\circ 40'$ and $110:\bar{1}\bar{1}0 = 59^\circ 50'$, which give to the crystals the appearance of obtuse rhombohedra. The form *o* is quite subordinate, and only found on a few individuals. None of the crystals lent themselves to accurate determination, for whilst the faces of *c* and *o* are fairly bright and smooth, those of the prism *p* are invariably much rounded, even on the smallest crystals. The angles and axial ratios given above are therefore to be regarded as rough approximations only, since the angle *cp* was the only one which could be satisfactorily measured. No definite creavage was observed. The extinction on *p* makes an angle of 26° with the edge *pc*.

The compound appears, therefore, to be ethylic acetoallylenedicarboxylate. This formula is supported by the action of aniline on the ethereal salt. Aniline dissolves it, and the solution, after being boiled for half an hour, and then acidified with hydrochloric acid, gives a dark red precipitate, which becomes yellow when washed with ether. It dissolves in hot dilute spirit, and, on cooling, crystallises in glittering, yellow plates, melting at 180° .

The analytical numbers agree with the formula $C_{17}H_{19}NO_4$.

0.1882 gave 0.4650 CO_2 and 0.1082 H_2O . $C = 67.38$; $H = 6.42$.

0.3124 „ 12 c.c. moist nitrogen at 26° and 755 mm. $N = 4.23$.

0.2980 „ 11.5 „ „ „ „ 20° „ 763 „ . $N = 4.43$.

$C_{17}H_{19}NO_4$ requires $C = 67.77$; $H = 6.31$; $N = 4.65$ per cent.

The substance is readily soluble in alcohol, insoluble in water, and is decomposed by boiling hydrochloric acid with formation of aniline; it therefore resembles anilpyrroacemic acid in its properties. The formula of such a compound from the ethereal salt, $C_{11}H_{14}O_5$, excludes the formula brought forward before, and points to the view that it is to be regarded as ethylic acetoallylenedicarboxylate. The constitution of the substance formed from it under the influence of aniline is, therefore,

The view with regard to the constitution of the acid, $C_6H_6O_3$, resulting from the hydrolysis of the ethereal salt of the formula $C_{11}H_{14}O_5$, requires also to be modified. For this acid, there are various formulæ possible; the expression $CH_3 \cdot CO \cdot CH : C : CH \cdot COOH$, which at first would seem probable, does not explain the behaviour of the compound described before (*loc. cit.*, p. 1394). The properties of the acid are so similar to those of coumalic acid, that one might assign to it an analogous constitution—such as $CH_3 \cdot C \begin{array}{l} \swarrow \text{CH} \cdot C(OH) \\ \searrow O \text{---} CO \end{array} CH$, and regard it as methylhydroxycoumalin.

This substance is readily etherified by saturating its solution in methylic alcohol with hydrogen chloride. The liquid is allowed to stand overnight, then poured into ice-cold water, extracted with ether, and the unchanged organic acid removed by dilute sodium carbonate. On evaporating the ether, an oil remains, which solidifies after some time. It crystallises from ether in colourless plates, melting at 139 – 140° , and is hydrolysed on boiling with water.

Analysis of the compound, dried in a vacuum over sulphuric acid, gave numbers agreeing with the formula $C_6H_5(CH_3)O_3$.

0.2135 gave 0.4694 CO_2 and 0.1065 H_2O . $C = 59.96$; $H = 5.54$.

0.2070 „ 0.4525 „ „ 0.1040 „ . $C = 59.62$; $H = 5.58$.

$C_7H_8O_3$ requires $C = 60.0$; $H = 5.71$ per cent.

Assuming that the constitution of the compound $C_6H_6O_3$ is to be expressed by the above formula, it would follow that the etherification is not brought about by an opening of the coumalin ring, unless, at the same time, a transformation takes place which leads to the formation of methylic acetoallylenecarboxylate, $CH_3 \cdot CO \cdot CH : C : CH \cdot COOCH_3$.

Experiments with the view of solving this question are in progress.

Action of Ethylic α -Chlorocrotonate on Ethylic Benzoylacetate.

This is quite analogous to the behaviour of the former ethereal salt towards ethylic acetoacetate. The reaction is carried out in the usual manner, by mixing ethylic benzoylacetate with the calculated quantity of sodium dissolved in absolute alcohol, and gradually adding the equivalent amount of ethylic α -chlorocrotonate. The mixture is boiled on the water bath in a flask until it is no longer alkaline, using a reflux condenser; the alcohol is then evaporated, the residue poured into water, and the ethereal salt extracted with ether. The oil remaining after removal of the ether boils at $195-200^\circ$ under a pressure of 10 mm., and has the density $d_{15^\circ/15^\circ} = 1.1361$. It is of a pale yellow colour, and its alcoholic solution turns faintly red on the addition of ferric chloride.

On analysis, the following numbers were obtained.

0.2000 gave 0.4960 CO_2 and 0.1218 H_2O . $C = 67.27$; $H = 6.67$.

$C_{17}H_{20}O_5$ requires $C = 67.10$; $H = 6.57$ per cent.

According to the former view concerning the action of the ethereal salts of chlorofumaric and α -chlorocrotonic acids on those of β -ketonic acids, this substance is to be regarded as ethylic benzoyl- β -butylenedicarboxylate. Its constitution, in the light of Claisen's researches on ketone-compounds, is to be represented by the formula

This expression is confirmed by the determination of the refractive index, which was found to be $n_D = 1.524$ at 15° ; the molecular refraction amounts, therefore, to 81.80, whilst the value calculated for the above formula is 81.53.

Ethylic Malonyl- β -butylenetricarboxylate.

This compound is formed by adding 20 grams of ethylic acetonedicarboxylate, and then 15 grams of ethylic α -chlorocrotonate, to a solution of 2.3 grams of sodium dissolved in 50 c.c. of absolute alcohol, and by boiling the mixture on the water bath until it is no longer alkaline to litmus paper. The product of the reaction, isolated in the usual way, boils at $196-197^\circ$ under a pressure of 10 mm.; it is a

colourless oil, having the density $d_{15^\circ/15^\circ} = 1.1445$, and its alcoholic solution is only faintly coloured by ferric chloride.

Analysis gave values corresponding with the formula for ethylic malonyl- β -butylenetricarboxylate.

0.2471 gave 0.5190 CO_2 and 0.1566 H_2O . $\text{C} = 57.28$; $\text{H} = 7.04$.

$\text{C}_{15}\text{H}_{22}\text{O}_7$ requires $\text{C} = 57.32$; $\text{H} = 7.00$ per cent.

The constitution of this compound, indicated above, is confirmed by its refractometric behaviour. The refractive index was found to be $n_D = 1.472$ at 15° ; the expression $M \frac{n^2 - 1}{(n^2 + 2)d}$ amounts, therefore, to 76.76, whilst the formula $\text{C}_{15}\text{H}_{22}\text{O}_3 \cdot (\text{O}_3)^n$ requires 76.54.

Action of Ammonia.—If the ethereal salt is allowed to remain in contact with a concentrated aqueous solution of ammonia for several days, it disappears, and from the yellow solution, which, on exposure to the air, turns bluish-green, a crystalline solid separates; this dissolves in boiling water, and, on cooling, comes down in colourless, striated, octagonal plates, which melt at $199\text{--}200^\circ$, having begun to soften a few degrees before.

0.2149 gave 0.4095 CO_2 and 0.1196 H_2O . $\text{C} = 51.54$; $\text{H} = 6.18$.

0.0986 „ 9.2 c.c. moist nitrogen at 19° and 765 mm.; $\text{N} = 10.80$.

$\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_5$ requires $\text{C} = 51.56$; $\text{H} = 6.25$; $\text{N} = 10.93$ per cent.

The compound is therefore to be represented by one of the following formulæ.

The aqueous mother liquor of the compound melting at $199\text{--}200^\circ$ contains, besides this substance, another crystallising in needles, the isolation of which could not be effected. This mixture has not a constant melting point, beginning to soften at 165° . Its analysis leads to the same composition, $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_5$, as was established for the substance crystallising in plates.

0.2020 gave 0.3790 CO_2 and 0.1160 H_2O . $\text{C} = 51.17$; $\text{H} = 6.38$

0.2047 „ 20 c.c. moist nitrogen at 18° and 758 mm.; $\text{N} = 11.10$.

The action of ammonia on the ethereal salt also gives rise to a third substance; this occurs in the ammoniacal filtrate from the solid con-

sisting of the two above-mentioned amides, and is precipitated either on acidifying the solution with hydrochloric acid, or on evaporating it. This compound is the diamido-acid, corresponding with one of the three isomeric ethereal salts symbolised above. The acid being insoluble in water and in alcohol, and only slightly soluble in glacial acetic acid, is purified by decolorising its solution in ammonia with animal charcoal, and precipitating the filtrate with hydrochloric acid; it is a grey, crystalline powder which does not melt, but decomposes at about 270° . The analytical data agree with the formula $C_9H_{12}N_2O_5$.

0.2038 gave 0.3526 CO_2 and 0.0954 H_2O . $C = 47.19$; $H = 5.20$.

0.2110 „ 22 c.c. moist nitrogen at 18° and 774 mm.; $N = 12.26$.

$C_9H_{12}N_2O_5$ requires $C = 47.37$; $H = 5.26$; $N = 12.28$ per cent.

It may be mentioned that the research recorded in this paper is being extended to the study of the action of ethylic chlorofumarate and ethylic α -chlorocrotonate on the ethereal salts of other β -ketonic acids.

In conclusion, I must express my thanks to Dr. C. Wolf for the help he has given me in the analytical part of this work.

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