LXXII.—*The Action of Phenylpropiolyl Chloride on Ketonic Compounds. Part II.*

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IN a recent communication made to the Society in conjunction with R. W. Merriman (*Trans.*, 1905, **87**, 1383), it has been shown that phenylpropiolyl chloride interacts with sodioacetylacetone to form a yellow compound, which was represented by the formula

This substance, under the influence of piperidine, is transformed into the red isomeride:

which dissolves in alkalis or their carbonates, as well as in organic bases, to yield blue solutions; on boiling with sodium carbonate, it changes into a colourless acid which has the same molecular composition and which was formulated thus:

I have subjected these compounds to a closer study in order to supply further evidence for the correctness of the above formulæ, and, although this task has not been fully accomplished, yet on account of

the interesting results obtained up to the present I have thought it advisable to place them on record.

Attention has been especially directed to the examination of the red isomeride, $C_{14}H_{12}O_3$, since its properties, as previously stated, closely resemble the compound obtained from ethyl oxaloacetate (see Ruhe-mann and Hemmy, *Trans.*, 1897, 71, 34) and oxalyldibenzylketone, which Claisen and Ewan (*Annalen*, 1895, 284, 245) prepared by the action of sodium ethoxide on a mixture of dibenzylketone and ethyl oxalate. The latter substance had been carefully investigated by its discoverers, and the constitution which they derived from the study of this compound closely agrees with the formulæ of the other two substances with similar properties, as indicated by the following symbols:

Although this fact may be regarded as a sufficient proof for the formula of the red compound $C_{14}H_{12}O_3$, yet I have thought it advisable to support this evidence by an investigation of the substance on lines similar to those followed up by Claisen and Ewan in the case of oxalyldibenzylketone. Like this substance, the red isomeride $C_{14}H_{12}O_3$ interacts with one molecule of phenylhydrazine only to yield a phenylhydrazone. The circumstance that it is insoluble in alkalis leads to the conclusion that the compound is to be represented thus:

and that its formation is accompanied by the change of the enolic into the ketonic group. The behaviour of the red substance towards semicarbazide is analogous, as a semicarbazone is produced, which on account of its insolubility in caustic soda must be expressed by the symbol:

The fact that this compound is colourless is of additional interest, because it indicates that the red colour of the substance $C_{14}H_{12}O_3$ is due to the enolic grouping and disappears with the transformation

* I have adopted this name instead of the one used before (*loc cit.*) in order to indicate the relation of this compound to the other two substances.

into the ketonic group. The product of the action of hydroxylamine on the red compound points to the same conclusion, since the colourless oxime,

which, indeed, dissolves in sodium carbonate, yields a light yellow solution.

This behaviour of the red compound $\text{C}_{14}\text{H}_{12}\text{O}_3$ allows of a ready explanation of the results at which Claisen and Ewan (*loc. cit.*) arrived in the course of their investigation of oxalyldibenzylketone. These chemists have found that this substance forms with caustic soda a yellow salt, and blue solutions with an excess of the alkali. The metallic derivatives which are thus produced they represent by the formulæ :

The action of alkalis on the red substance $\text{C}_{14}\text{H}_{12}\text{O}_3$ leads to the conclusion that the blue salt is to be represented thus :

because the grouping $\text{:C}(\text{OH}) \cdot \text{CO}$ — contained in the compound $\text{C}_{14}\text{H}_{12}\text{O}_3$, as well as in ethyl oxalylaconitate, gives rise to the formation of blue salts. On the other hand, the yellow sodium derivative of oxalyldibenzylketone is to be expressed by the formula :

in which the ketonic group occupies the β -position with respect to the enolic group. It would therefore follow that the former arrangement leads to the formation of blue salts, whilst the other grouping yields yellow salts. At present, there exist only the three above-mentioned compounds which contain the group $\text{:C}(\text{OH}) \cdot \text{CO}$ — and which form blue

salts,* but a number of substances of the type $\text{:C}(\text{OH}) \cdot \overset{\text{CO}}{\underset{|}{\text{C}}} \text{CO}$ — are known, and they all dissolve in alkalis or their carbonates to yield yellow solutions ; the following may be mentioned as members of this series : benzoylacetylacetone, $\text{}^6\text{H}_5 \cdot \text{CO} \cdot \text{C}(\text{CO} \cdot \text{CH}_3) : \text{C}(\text{OH}) \cdot \text{CH}_3$; di-

* A similar compound is most probably formed by the action of sodium acetate and acetic anhydride on ethyl acetonylacetate when a violet solution is produced (see Claisen and Stylos, *Ber.*, 1889, 22, 1141). I am engaged in the study of this reaction.

benzoylacetone, $(C_6H_5 \cdot CO)_2C:C(OH) \cdot CH_3$, and xanthochelidonic acid, $CO[CH:C(OH) \cdot CO_2H]_2$.

The view which I have advanced concerning the constitution of the blue sodium derivative of oxalyldibenzylketone is in complete harmony with the behaviour of the ketonic compound itself. According to Claisen and Ewan, the blue salt interacts with methyl iodide to yield a methyl derivative, which dissolves in alkalis, forming yellow solutions, and, on hydrolysis, furnishes dibenzylmethylketone. It follows, therefore, that this oxalyldibenzylmethylketone has the formula :

and that its formation is analogous to the production of ethyl methyl-acetoacetate.

An isomeric methyl derivative has been obtained by Claisen and Ewan (*loc. cit.*) on treatment of the silver derivative of oxalyldibenzylketone with methyl iodide. The facts that this compound gives with alkalis blue solutions and, on hydrolysis, furnishes oxalyldibenzylketone lead to the symbol :

a similar structure should be attributed to the acetyloxalyldibenzylketone :

which forms a violet potassium salt.

The properties of the phenylhydrazone and the oxime agree with the formulæ :

The analogous constitution must be assigned to the amino- and anilino-derivatives of the oxalyl compound.

It has previously been pointed out (see Rubemann and Merriman, *loc. cit.*) that the properties of the direct product of the action between phenylpropionyl chloride and acetylacetone differ most markedly from those of its red isomeride. This difference is also manifested by the behaviour towards phenylhydrazine, because an almost colourless substance is formed, the solutions of which are light yellow. The analytical data indicate that two molecules of phenylhydrazine are required for the formation of this substance and that the reaction takes place according to the equation

The constitution of this compound should most probably be represented thus: $\text{C}(\text{C}_6\text{H}_5):\text{C}(\text{NH}\cdot\text{NHPh})\cdot\text{C}\cdot\text{N}\cdot\text{NHPh}$. The mode of its formation would therefore be similar to the transformation of the yellow substance $\text{C}_{14}\text{H}_{12}\text{O}_3$ into its red isomeride.

EXPERIMENTAL.

The Phenylhydrazone of Acetyloxalylphenylmethylpropene.

On adding phenylhydrazine, dissolved in 50 per cent. acetic acid, to the cold solution of the red compound $\text{C}_{14}\text{H}_{12}\text{O}_3$ in methyl alcohol, a deep red coloration takes place which is no doubt due to the formation of a salt. The colour, after a short time, changes to yellowish-red and a solid is deposited. This product is very soluble in chloroform, sparingly so in ether, but readily dissolves in hot alcohol, and, on cooling, crystallises in yellow plates which melt and decompose indefinitely at 169—171°.

0.2023 gave 0.5595 CO_2 and 0.1032 H_2O . $\text{C} = 75.42$; $\text{H} = 5.66$.

0.2157 „ 16.2 c.c. moist nitrogen at 20° and 768 mm. $\text{N} = 8.69$.

$\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}_2$ requires $\text{C} = 75.47$; $\text{H} = 5.66$; $\text{N} = 8.80$ per cent.

The phenylhydrazone is insoluble in alkalis or their carbonates; it dissolves in concentrated sulphuric acid yielding a deep red solution.

The Oxime of Acetyloxalylphenylmethylpropene.

This substance is formed on adding a mixture of equivalent quantities of hydroxylamine hydrochloride and sodium carbonate, dissolved in water, to the alcoholic solution of the red compound $\text{C}_{14}\text{H}_{12}\text{O}_3$. The solution develops a deep red colour which rapidly changes to a light yellow. The mixture, after two days, is extracted with ether, when, after evaporation of the solvent, the oxime is left behind as a slightly coloured oil which shortly sets to a solid. For purification it is dissolved in a little ether and the solution mixed with light petroleum, when colourless prisms gradually separate which melt indefinitely at 129—130°.

0.2009 gave 0.5068 CO_2 and 0.0991 H_2O . $\text{C} = 68.80$; $\text{H} = 5.48$.

0.2233 „ 11.8 c.c. moist nitrogen at 20° and 755.5 mm. $\text{N} = 6.0$.

0.1725 gave 8.8 c.c. moist nitrogen at 20° and 759 mm. $\text{N} = 5.83$.

$\text{C}_{14}\text{H}_{13}\text{O}_3\text{N}$ requires $\text{C} = 69.13$; $\text{H} = 5.35$; $\text{N} = 5.76$ per cent.

The oxime dissolves freely in ether or alcohol, but only sparingly in boiling water; it is readily soluble in sodium carbonate, forming a yellow solution from which the oxime is reprecipitated by hydro-

chloric acid as well as by acetic acid. The alcoholic solution of the oxime yields with ferric chloride an olive-green coloration.

The Semicarbazone of Acetyloxalylphenylmethylpropene.

On adding the mixture of equal weights of semicarbazide hydrochloride and potassium acetate, dissolved in water, to an alcoholic solution of the red substance $C_{14}H_{12}O_3$, a dark coloration in this case, also, takes place which quickly becomes light red. After standing overnight, water is added, when a white solid is precipitated which is insoluble in water, benzene, or ether, but dissolves in boiling alcohol, although with great difficulty, and, on cooling, gradually separates in colourless prisms. The semicarbazide is readily soluble in warm glacial acetic acid and is precipitated by water in small crystals which melt and decompose at 208° .

0.2055 gave 0.4760 CO_2 and 0.0998 H_2O . $C = 63.17$; $H = 5.39$.

0.2160 „ 27.8 c.c. moist nitrogen at 20° and 769 mm. $N = 14.89$.

$C_{15}H_{15}O_3N_3$ requires $C = 63.16$; $H = 5.26$; $N = 14.74$ per cent.

Action of Phenylhydrazine on Acetylmethylbenzylideneketodihydrofurfuran.

The yellow substance $C_{14}H_{12}O_3$, which is formed by the action of sodioacetylacetone on phenylpropyl chloride when treated in alcoholic solution with phenylhydrazine dissolved in acetic acid, yields a deep red coloration which rapidly changes to yellowish-red. The mixture slowly deposits a solid which is readily soluble in hot alcohol and, on cooling, crystallises in almost colourless needles which melt and decompose at $161-162^\circ$.

0.1240 gave 0.3468 CO_2 and 0.0698 H_2O . $C = 76.27$; $H = 6.25$.

0.2013 „ 24 c.c. moist nitrogen at 20° and 769.5 mm. $N = 13.81$.

0.2197 „ 26.4 c.c. moist nitrogen at 21° and 769.5 mm. $N = 13.85$.

$C_{26}N_{24}ON_4$ requires $C = 76.47$; $H = 5.88$; $N = 13.72$ per cent.

On adding concentrated sulphuric acid to this compound, it first turns yellowish-red, and then dissolves, yielding a bluish-green solution which gradually changes to yellow. On warming the compound with concentrated hydrochloric acid, it yields a yellow solution which rapidly becomes colourless.

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