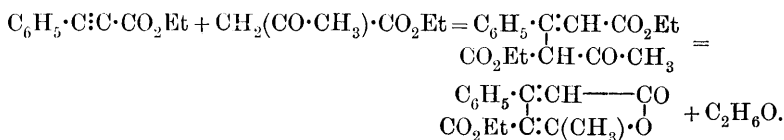


XLI.—*The Formation of 4-Pyrone Compounds from Acetylenic Acids. Part I.*

By SIEGFRIED RUHEMANN.

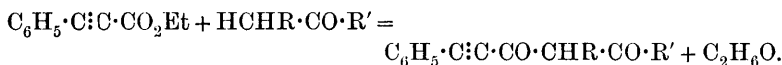
IN the course of my studies on the esters of acetylenic acids, it has been shown (Trans., 1899, 75, 245, 411) that, in the presence of sodium ethoxide, they condense with β -ketonic esters or β -diketones to form 2-pyrone derivatives. For example, ethyl phenylpropiolate reacts with ethyl acetoacetate, thus :



This reaction led to the knowledge of a number of 2-pyrone compounds which, under the influence of ammonia, were transformed into pyridine derivatives.

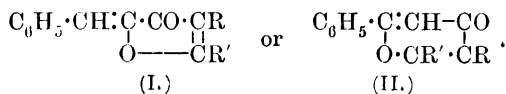
It appeared of interest to examine whether ketones with the grouping $\cdot\text{CH}_2\cdot\text{CO}\cdot$ would react with the esters of the acetylenic acids in a

manner similar to their action with ethyl oxalate, and yield acetylenic β -diketones:

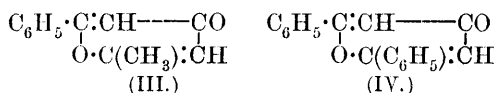


(R and R' denote hydrocarbon radicles.)

From previous work on the behaviour of organic bases towards acetylenic compounds (Ruhemann and Stapleton, *Trans.*, 1900, **77**, 239), it was to be expected that such diketones would condense to a five- (I) or a six- (II) membered ring:



It has been found that such a process actually takes place, and that the acetylenic diketones which, no doubt, are first formed condense according to (II) and yield 4-pyrone derivatives. This reaction has been applied to the preparation of 2-phenyl-6-methyl-4-pyrone (III)



and 2:6-diphenyl-4-pyrone (IV).

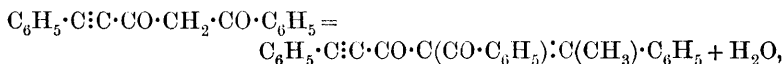
Feist (*Ber.*, 1890, **23**, 3726) showed that the latter compound is formed from dehydrobenzoylacetic acid in the same way as 2:6-dimethyl-4-pyrone is produced from dehydracetic acid. The description of the properties which he gives for this substance differ in one point only from my observations. Feist states that the pyrone derivative dissolves in cold concentrated sulphuric acid, yielding a colourless solution which exhibits a violet fluorescence. This phenomenon was not observed with the specimen described in the present work, but its solutions in sulphuric acid or in boiling concentrated hydrochloric acid are yellow. Oxonium salts are thus produced, which are decomposed by water into the acids and the colourless diphenyl-4-pyrone.

The hydrochloride of 2-phenyl-6-methyl-4-pyrone, however, is not dissociated by water, and this as well as the hydrochloride of the former pyrone derivative, with platinic chloride, yields platinic salts. The fluorescence of the solution of diphenyl-4-pyrone which Feist observed is probably caused by the presence of a trace of another compound formed together with the pyrone on heating dehydrobenzoylacetic acid with concentrated hydrochloric acid. This substance is probably identical with the compound which is produced along with the pyrone by the action of sodium ethoxide on a mixture of ethylphenylpropionate and acetophenone, and which dissolves in cold

sulphuric acid to yield a violet solution. It has the composition $C_{25}H_{20}O_3$, and is formed thus :

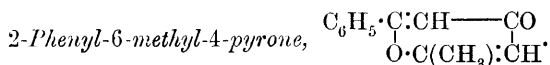


The constitution of the substance may be represented by the formula, $C_6H_5 \cdot CH_2 \cdot CO \cdot CO \cdot C(CO \cdot C_6H_5) : C(CH_3) \cdot C_6H_5$. Its formation can easily be explained by assuming that the acetylenic ester is first transformed into the acetylenic- β -diketone, which subsequently reacts with a second molecule of acetophenone, thus :



and that finally the water is added to the acetylenic grouping. Preference is given to this structure, because the other possible formulæ do not allow of an explanation of the fact that the compound is insoluble in either sodium carbonate or potassium hydroxide. The occurrence of this substance in the product of the action of hydrochloric acid on dehydrobenzoylacetic acid can readily be accounted for.

EXPERIMENTAL.



This substance is formed on adding to a suspension of dry sodium ethoxide (6.8 grams), in absolute ether, pure acetone (7 grams; prepared from its bisulphite compound), and then gradually ethyl phenylpropionate (17.4 grams). The mixture, which after a short time sets to a semi-solid, is kept for a day and then treated with water, when the solid dissolves. The ethereal layer, which contains only a very small quantity of a red oil, is separated from the aqueous solution, the latter is mixed with an excess of dilute sulphuric acid, and extracted with ether. On evaporation of the ether, a dark oil is left behind, which contains phenylpropionic acid besides the pyrone. Without removing the acid by sodium carbonate, the oil may be distilled in a vacuum; at first, carbon dioxide is evolved and phenylacetylene passes over, and then at $220-225^\circ$ under a pressure of about 14 mm. phenylmethyl-4-pyrone distils as a yellow oil which soon solidifies. The compound is readily soluble in alcohol; on adding water to this solution, an emulsion is produced from which crystals do not separate even on being kept for a day. It is also very soluble in benzene or ether, less so in cold, but readily so in hot, water; it dissolves only sparingly in boiling light petroleum, and, on cooling, crystallises in colourless needles, melting at $87-88^\circ$:

434 FORMATION OF 4-PYRONE COMPOUNDS FROM ACETYLENIC ACIDS.

0.2060 gave 0.5835 CO₂ and 0.1005 H₂O. C = 77.25 ; H = 5.42.

C₁₂H₁₀O₂ requires C = 77.42 ; H = 5.38 per cent.

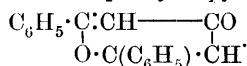
2-Phenyl-6-methyl-4-pyrone is very soluble in hydrochloric acid, yielding a hydrochloride which is not dissociated by water ; on adding platinic chloride to the solution in hydrochloric acid, yellow needles of the *platinichloride* are formed :

0.2317 gave 0.0572 Pt. Pt = 24.69.

(C₁₂H₁₀O₂)₂.H₂PtCl₆ requires Pt = 24.88 per cent.

Action of Acetophenone on Ethyl Phenylpropiolate.

On mixing the suspension of sodium ethoxide (6.8 grams) in dry ether with acetophenone (12 grams) and ethyl phenylpropiolate (17.4 grams), a dark red coloration is produced. The mixture, after being kept for two days, is poured into water, and the ethereal solution separated. This contains the compound C₂₅H₂₀O₃, which is described later. The aqueous layer is acidified with dilute sulphuric acid, and extracted with ether. On evaporation of the ether, a brown oil remains behind, which partly solidifies in the course of a few hours. The solid is 2:6-diphenyl-4-pyrone,



It is freed from the adhering oil by the aid of the pump, and washed with dilute alcohol until it is almost white. The substance is moderately soluble in cold, readily so in boiling, alcohol, and crystallises from dilute alcohol in colourless needles, which on heating behave in the manner stated by Feist (*loc. cit.*) ; they sinter at about 130°, and melt at 138—139° :

0.2068 gave 0.6220 CO₂ and 0.0933 H₂O. C = 82.02 ; H = 5.01.

0.2023 „ 0.6096 CO₂ „ 0.0891 H₂O. C = 82.18 ; H = 4.89.

C₁₇H₁₂O₂ requires C = 82.22 ; H = 4.84 per cent.

It has already been mentioned (p. 432) that diphenyl-4-pyrone is soluble in concentrated sulphuric acid and yields a yellow solution. The solution of the substance in hot hydrochloric acid has the same colour as, indeed, have the needles of the hydrochloride which separate on cooling ; in the presence of water, the crystals become colourless, owing to the dissociation of the salt into the acid and the pyrone.

On adding platinic chloride to the solution of diphenyl-4-pyrone in hot hydrochloric acid, orange prisms of the *platinichloride* are formed :

0.2625 gave 0.0562 Pt. Pt = 21.41.

{C₁₇H₁₂O₂}₂.H₂PtCl₆ requires Pt = 21.47 per cent.

The *compound*, $C_{25}H_{20}O_3$, which is contained in the ethereal solution of the product of the reaction between sodium ethoxide, acetophenone, and ethyl phenylpropionate, gradually separates before the ether is evaporated, and, on evaporation of the ether, is left behind as a dark solid; on washing with alcohol, it is obtained quite white. The substance is very soluble in chloroform, less so in cold, but readily so in hot, benzene; it dissolves very sparingly in boiling alcohol, and, on cooling, slowly crystallises in colourless prisms, melting at 224° :

0.2055 gave 0.6136 CO_2 and 0.1042 H_2O . $C = 81.43$; $H = 5.64$.

0.2003 „ 0.5985 CO_2 „, 0.0984 H_2O . $C = 81.53$; $H = 5.46$.

$C_{25}H_{20}O_3$ requires $C = 81.52$; $H = 5.43$ per cent.

The substance dissolves in cold concentrated sulphuric acid, yielding a violet solution; it is remarkably stable, and does not dissolve on boiling with hydrochloric acid or dilute potassium hydroxide. On heating with alcoholic potash, it is decomposed, but, besides acetophenone, only a resinous product is formed.

I am engaged in the further study of this compound with the view of examining whether the formula which I have suggested (p. 432) is correct. I propose, also, to investigate on similar lines the behaviour of ketones towards diethyl acetylenedicarboxylate.

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