CXXII.—*The Formation of 4-Pyrone Compounds from Acetylenic Acids. Part II.*

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RECENTLY (Trans., 1908, 98, 431) I have described a method of formation of 4-pyrone compounds, which is based on the reaction between ketones and ethyl phenylpropiolate in the presence of sodium ethoxide. Thus, two members of this group of substances have been obtained, namely, 2-phenyl-6-methyl-4-pyrone (I) and 2:6-diphenyl-4-pyrone (II) :

I have mentioned also (*loc. cit.*) that the formation of diphenylpyrone is accompanied by the production of a compound, $\text{C}_{25}\text{H}_{25}\text{O}_3$, which is characterised by the violet coloration of its solution in concentrated sulphuric acid. I have frequently studied the action of

sodium ethoxide on the mixture of acetone and ethyl phenylpropiolate without having been able to trace a compound with similar properties; the product of the reaction consists of phenylmethylpyrone, the yield of which amounts to 48—50 per cent., of the unchanged acetylenic ester, and the corresponding acid.

The present paper deals with the study of phenylmethylpyrone, which I have carried out on lines similar to those adopted by F. Feist (*Annalen*, 1890, **257**, 253) in his work on 2:6-dimethyl-4-pyrone. He showed that this compound, on treatment with baryta, is transformed into the yellow barium salt of diacetylacetone, which, with hydrochloric acid, yields the colourless triketone, $(\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2)_2 \text{CO}$. He has not been able to accomplish the analogous change on using diphenylpyrone owing to the insolubility of this pyrone in water (compare *Ber.*, 1890, **23**, 3726). I have repeated this experiment, but have also failed to isolate the triketone, dibenzoylacetone, from the product of the action of baryta on the pyrone. Phenylmethylpyrone, however, is readily transformed into a yellow barium salt, which, with hydrochloric acid, yields *benzoylacetylacetone*,

This compound resembles diacetylacetone in its behaviour. Feist has found (*loc. cit.*) that the latter triketone forms, with phenylhydrazine, a yellow diphenylhydrazone, which is produced, also, by the action of the hydrazine on 2:6-dimethyl-4-pyronecarboxylic acid; in this case, however, a colourless substance is formed at the same time which contains one molecule of water less than the dihydrazone. A compound, which in composition and properties resembles this substance, is produced on treatment of benzoylacetylacetone with phenylhydrazine. The fact that this compound is very stable and only slightly reduces Fehling's solution, even on boiling, points to the constitution:

This corresponds with the formula suggested by Feist for the colourless compound which is formed from dimethylpyronecarboxylic acid.

By the action of ammonia, benzoylacetylacetone is transformed into 2-phenyl-6-methyl-4-pyridone,

This substance has a characteristic behaviour which neither pyridone nor its dimethyl derivative seems to possess, namely, that its aqueous solutions readily gelatinise; this property renders its purification somewhat troublesome. I have prepared several salts of this base, but none of them exhibits this phenomenon. The ease with which β -diketones, for example, acetylacetone, react with aldehydes has

induced me to ascertain whether benzoylacetylacetone shows a similar behaviour ; I have found, however, that in the presence of neither piperidine nor sodium hydroxide as catalytic agent does this triketone condense with benzaldehyde or salicylaldehyde.

EXPERIMENTAL.

Benzoylacetylacetone, $C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$.

On adding a concentrated aqueous solution of baryta to phenylmethylpyrone dissolved in boiling water, a yellow barium salt is precipitated which, when added to dilute hydrochloric acid, loses its colour and is transformed into benzoylacetylacetone. This substance is sparingly soluble in carbon disulphide, ether, or cold alcohol, but readily dissolves in boiling alcohol or chloroform ; it crystallises from light petroleum, in which on boiling it is fairly soluble, in pale brown needles melting at $106-107^\circ$:

0.2213 gave 0.5716 CO_2 and 0.1182 H_2O . $C = 70.44$; $H = 5.93$.

$C_{12}H_{12}O_3$ requires $C = 70.59$; $H = 5.88$ per cent.

The triketone is readily dissolved by dilute potassium hydroxide, yielding a yellow solution ; it is insoluble in cold, but soluble in hot sodium carbonate solution.

Action of Phenylhydrazine on Benzoylacetylacetone.

On adding water to the mixture of the triketone (1 gram), dissolved in alcohol, and phenylhydrazine (1.2 grams), an oily product is precipitated which, when stirred with alcohol, sets to a yellow solid. This is sparingly soluble in boiling alcohol, and, on cooling, crystallises in colourless prisms melting at $174-175^\circ$:

0.2015 gave 0.5800 CO_2 and 0.1100 H_2O . $C = 78.50$; $H = 6.06$.

0.2265 „ 30 c.c. N_2 (moist) at 17° and 756 mm. $N = 15.28$.

$C_{24}H_{22}N_4$ requires $C = 78.69$; $H = 6.01$; $N = 15.30$ per cent.

The formation of this substance is most probably proceeded by the production of the diphenylhydrazone of benzoylacetylacetone, which, however, at once condenses with loss of water. The fact that this compound is but slightly attacked by potassium hydroxide or hydrochloric acid, and only faintly reduces Fehling's solution on boiling, seems to support the formula given on p. 1282.

Benzoylacetylacetone is readily soluble in hot, concentrated ammonia; on evaporating the solution on the water-bath, a solid is left behind which is sparingly soluble in cold, but readily so in boiling water. The hot concentrated solution, after treatment with animal charcoal, deposits colourless, curved needles, and the mother liquor, after a short time, sets to a jelly which renders it impossible to collect the crystals. It is therefore necessary to filter them from the warm solution. The pyridone melts at 177—178°:

0.2100 gave 0.5970 CO₂ and 0.1155 H₂O. C = 77.53; H = 6.11.

0.2230 „ 14.8 c.c. N₂ (moist) at 18° and 755 mm. N = 7.61.

C₁₂H₁₁ON requires C = 77.84. H = 5.95; N = 7.57 per cent.

The gelatinous product which separates from the mother liquor of the crystals seems to contain the same substance; this would follow from the fact that the solid which is left behind, on evaporation to dryness, gave the following analytical data:

0.2172 gave 0.6138 CO₂ and 0.1182 H₂O. C = 77.07; H = 6.04,

which do not appreciably differ from those required for phenylmethylpyridone.

The pyridone dissolves in hot, concentrated hydrochloric acid, and the solution, on cooling, deposits colourless needles of the *hydrochloride*. This melts at 242°, after having begun to soften at 225°; it is not very soluble in cold, but readily so in boiling water:

0.2340 gave 0.1518 AgCl. Cl = 16.05.

C₁₂H₁₁ON.HCl requires Cl = 16.03 per cent.

On adding platinum tetrachloride to the aqueous solution of the hydrochloride, the *platinichloride* of the pyridone is precipitated in pale orange, microscopic needles:

0.3048 gave 9.6 c.c. N₂ (moist) at 19° and 764 mm. N = 3.65.

0.2068 left on ignition 0.0520 Pt. Pt = 25.09.

(C₁₂H₁₁ON)₂.H₂PtCl₆ requires N = 3.59. Pt = 24.94 per cent.

The *picrate* is formed on mixing aqueous solutions of phenylmethylpyridone and picric acid. The emulsion which is first produced, soon sets to a crystalline solid, which is sparingly soluble in cold, but fairly readily in boiling water, and, on cooling, separates in yellow needles melting at 194—195°:

0.1986 gave 24 c.c. N₂ (moist) at 20° and 753 mm. N = 13.59.

C₁₂H₁₁ON.C₆H₃O₇N₃ requires N = 13.52 per cent.

The *chromate* is precipitated in orange needles on adding chromic acid, dissolved in water, to the aqueous solution of the pyridone :

0.2368 gave 10 c.c. N_2 (moist) at 19° and 754 mm. $N = 4.81$.

$(C_{12}H_{11}ON)_2 \cdot H_2Cr_2O_7$ requires $N = 4.75$ per cent.

The salt does not melt, but, on heating, begins to blacken at about 155° ; it is sparingly soluble in cold, but readily so, in boiling water.

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