LXXII.—*An Isomeric Change of Dehydracetic Acid.*

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RECENTLY it was noticed during the preparation of a large quantity of triacetic lactone, that if sulphuric acid of about 85 instead of 90 per cent. strength was used, the yield of triacetic lactone was considerably reduced. The triacetic lactone is prepared by heating dehydracetic acid with sulphuric acid of about 90 per cent. for a short time to 135° (Collie, Trans., 1891, **59**, 607). The product is then poured into water and the triacetic lactone crystallises out. When 85 per cent. sulphuric acid is used only a small quantity of the lactone separates when the product of the reaction is poured into water, but a further crop of crystals can be obtained by nearly neutralising the acid solution with solid sodium carbonate. At first these were thought to be impure triacetic lactone, but after purification by several recrystallisations they were found to have a melting point 99°, whilst the lactone melts at 189°.

The crystals were acid to litmus paper, and more soluble in water than triacetic lactone.

On analysis, the mean of three concordant results was:

$C = 56{\cdot}8$. $H = 4{\cdot}9$;

$(C_2H_2O)_n$ requires $C = 57{\cdot}1$; $H = 4{\cdot}8$ per cent.

On titration with soda the mean of several experiments gave the equivalent of the acid as 165. This is too high for triacetic lactone, $C_6H_6O_3 = 126$, but it agrees well with $C_8H_8O_4 = 168$.

The molecular weight was determined by the boiling point method, the molecular weight of 169 was obtained as the mean of three experiments.

From these results the compound is obviously isomeric with dehydracetic acid.

When boiled with hydrochloric acid it is decomposed into dimethylpyrone and carbon dioxide. From 1 gram of the acid 0·75 gram of dimethylpyrone was obtained. The dimethylpyrone was identified by its melting point, 132°, its yellow barium salt, and the production of diacetylacetone, which gives a blood-red coloration with ferric chloride,

$$C_8H_8O_4 = C_7H_8O_2 + CO_2.$$

By heating the compound to about 200°, it decomposed in an exactly similar manner, an almost quantitative yield of carbon dioxide and dimethylpyrone being produced. When boiled with excess of strong baryta solution it gave no yellow compound, but after a short time a barium salt crystallising in needles separated from the hot solution; these were filtered off, and in the filtrate, which had a strong odour of acetone, an acetate was found.

The barium salt on analysis gave Ba = 53·9; this agrees with the percentage of barium in barium malonate:

$C_3H_2O_4Ba,H_2O$ requires Ba = 53·3 per cent.

That the salt was barium malonate was proved by the fact that the free acid from the barium salt on heating gave carbon dioxide and acetic acid.

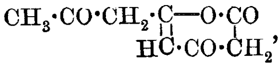
The electrical conductivity of the acid was found to be K = 0·00152.

The acid seems, therefore, to be in most respects identical with an acid obtained by Feist (*Annalen*, 1890, **257**, 253) by the action of sulphuric acid on the dichloride of dehydracetic acid. The chief difference was in the electrical conductivity, which Feist found to be K = 0·0385.

Several salts of the acid were prepared from a solution of the sodium salt. Silver nitrate gives a white precipitate soluble in hot water; mercuric chloride, a white precipitate; mercurous nitrate, a grey precipitate, which decomposes on warming and evolves carbon dioxide; ferric chloride, a dark yellow coloration and a slight precipitate on boiling: this, however, may be due to the decomposition of the sodium salt, for it was found that on boiling the sodium salt the solution became distinctly alkaline, and when acid was added, dehydracetic acid was precipitated. The dehydracetic acid melted at 108°, and when viewed under the microscope it was identical with the ordinary acid. Considerable decomposition, however, took place, as well as the change of the acid back to dehydracetic acid, for when a solution of the sodium salt was evaporated to half its bulk the distillate was found to contain acetylacetone, which gave a deep blood-red coloration with ferric chloride.

The free acid when heated in a sealed tube with strong ammonia gave an ammonium salt of a lutidonecarboxylic acid; the free acid melted at 258° and was the same as an acid obtained from ethyl *β*-aminocrotonate by heat (Collie, *Annalen*, 1884, **226**, 297). When heated, it decomposed quantitatively into 2 : 6-dimethylpyridone.

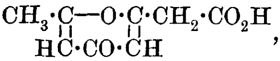
This interesting isomeric change of dehydracetic acid, when heated with sulphuric acid, to a pyronecarboxylic acid, and the reverse change when heated with soda may be expressed as follows:



$$\begin{array}{l} CH_3\cdot CO\cdot CH_2\cdot \overset{}{C}\!-\!O\cdot CO \\ \,\| \qquad\quad | \\ HC\cdot CO\cdot CH_2 \end{array}$$

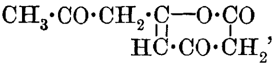
, dehydracetic acid.

$CH_3\cdot C(OH){:}CH\cdot CO\cdot CH{:}C(OH)\cdot CH_2\cdot CO_2H$, intermediate compound in acid solution.



$$\begin{array}{l} CH_3\cdot \underset{\Vert}{C}{-}O\cdot \underset{\Vert}{C}\cdot CH_2\cdot CO_2H \\ \quad HC\cdot CO\cdot CH \end{array}$$, 2-methylpyrone-6-acetic acid.

$CH_3\cdot CO\cdot CH_2\cdot C(OH){:}CH\cdot CO\cdot CH_2\cdot CO_2Na$, intermediate compound in alkaline solution.



$$\begin{array}{l} CH_3\cdot CO\cdot CH_2\cdot \underset{\Vert}{C}{-}O\cdot \underset{|}{C}O \\ \qquad\qquad\quad HC\cdot CO\cdot CH_2 \end{array}$$, dehydracetic acid.

The above formula easily explains the formation of a lutidonecarboxylic acid and also the formation of malonic acid, acetone, and acetic acid when the acid is heated respectively with ammonia or with concentrated baryta solution.

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