

CCCLXXIII.—*The Action of Tolyldiazines upon Dihydroxytartaric Acid.*

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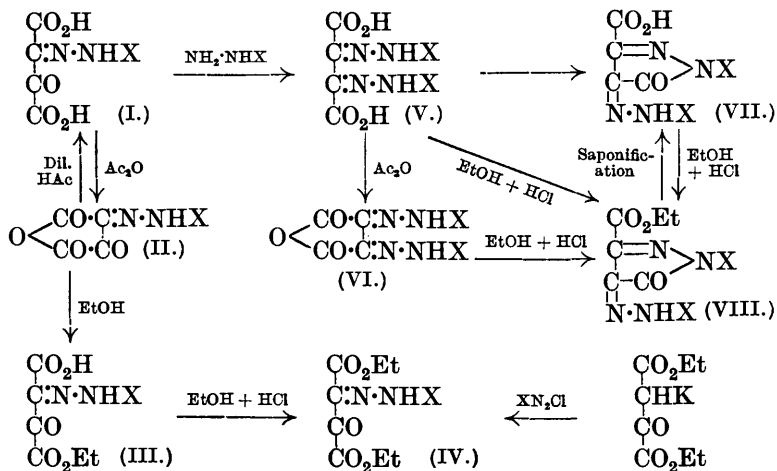
ALTHOUGH the osazones of dihydroxytartaric acid have been thoroughly investigated, its monohydrazones have never been prepared in a pure condition. Gnehm and Benda (*Annalen*, 1897, 299, 100) showed that the action of *p*-nitrophenylhydrazine upon excess of dihydroxytartaric acid yielded the pure osazone with no trace of a monohydrazone, whilst phenylhydrazine gave a mixture of the monohydrazone and osazone, which they did not separate into the two constituents. The action of halogen-substituted phenylhydrazines results in the formation of similar mixtures (this vol., p. 1323).

The action of *o*- and *p*-tolylhydrazines upon dihydroxytartaric acid differs from that of other hydrazines in that pure monohydrazones are readily obtained. These are well-crystallised, yellow solids, which, like the corresponding osazones, are converted into deep red acid anhydrides on heating with acetic anhydride. On crystallising these anhydrides from dilute acetic acid, the original hydrazones are re-formed; similarly, on crystallising the anhydrides from anhydrous alcohol, half-esters are formed. The second carboxyl group undergoes esterification only with difficulty, requiring prolonged boiling with alcohol containing hydrogen chloride; the diethyl ester thus formed may also be obtained by coupling diazotised toluidine with the potassium derivative of ethyl oxalacetate.

The most important property of the osazones of dihydroxytartaric acid is the ease with which they lose a molecule of water to give pyrazoline derivatives. This property is completely absent from the monohydrazones, and all attempts to cause pyrazoline ring formation have been unsuccessful.

The *o*- and *p*-tolyllosazones of dihydroxytartaric acid behave in the normal manner. They are sparingly soluble substances which cannot be crystallised unchanged from any solvent. They are converted into deep red anhydrides by heating with acetic anhydride, and into hydrazones of diketopyrazolinecarboxylic acids by crystallisation from acetic acid or by acidification of their sodium salts. In the former reaction, varying amounts of the isomeric anhydrides are simultaneously produced. These pyrazoline derivatives undergo esterification with difficulty and their esters are more easily obtained from the corresponding osazone.

The following scheme represents the reactions, X denoting the tolyl group :



EXPERIMENTAL.

Diketosuccinic acid o-tolyldiazone (I) was prepared by adding a solution of 26 g. of sodium dihydroxytartrate (1 mol.) in 180 c.c. of moderately concentrated hydrochloric acid (1 : 1) to a solution of 16 g. of *o*-tolyldiazine hydrochloride (1 mol.) in 1000 c.c. of very dilute hydrochloric acid (1 : 100). The *hydrazone* separated slowly as a deep yellow, crystalline powder, which was filtered off after 3—4 hours and crystallised from 75% acetic acid, in which it was moderately easily soluble and from which it separated in yellow, elongated, flat prisms, m. p. 192° (decomp.) (Found : N, 11.2. $\text{C}_{11}\text{H}_{10}\text{O}_5\text{N}_2$ requires N, 11.2%).

This *hydrazone* shows no tendency to lose water to form a pyrazoline derivative. It dissolves readily in hot sodium hydroxide solution and is reprecipitated on acidification. On boiling with acetic acid, partial conversion into the anhydride occurs, whilst boiling with alcohol containing hydrogen chloride causes esterification only.

Anhydrodiketosuccinic Acid o-Tolyldiazone (II).—The *hydrazone* (I) was added to boiling acetic anhydride until no more would dissolve. A clear, deep red solution was thus obtained which on cooling deposited the *anhydride* in long, red, glistening prisms, m. p. 208° (decomp.) (Found : N, 12.2. $\text{C}_{11}\text{H}_8\text{O}_4\text{N}_2$ requires N, 12.1%).

Ethyl Hydrogen Diketosuccinate o-Tolyldiazone (III).—The

above anhydride was boiled with anhydrous alcohol and the yellow solution thus obtained, on cooling, deposited the half-ester in yellow, irregular, thin plates, m. p. 115° (Found: N, 9.9. $C_{13}H_{14}O_5N_2$ requires N, 10.1%).

The half-ester may also be prepared by boiling the hydrazone (I) with alcohol containing 5% of dry hydrogen chloride for $\frac{1}{2}$ hour.

A definite formula cannot be assigned to this ester, as there is nothing to indicate which of the two carboxyl groups is esterified. The product appears not to be a mixture; its melting point is not changed by recrystallisation, and the fact that the second group can be esterified only with great difficulty points to a particular one being concerned in the first reaction.

Ethyl Diketosuccinate o-Tolylhydrazone (IV).—Although one carboxyl group of diketosuccinic acid *o*-tolylhydrazone is readily esterified, the diethyl ester was formed only by boiling the half-ester for 12 hours with alcohol saturated with dry hydrogen chloride. A certain amount of decomposition and tar formation occurred, and a dark brown solution was obtained, which on cooling deposited the *diethyl* ester in bright yellow, hexagonal plates or flattened prisms, m. p. 90° (Found: N, 9.1. $C_{15}H_{18}O_5N_2$ requires N, 9.15%).

The same ester was prepared by adding slowly a cold aqueous solution of *o*-toluenediazonium chloride (1 mol.) to an aqueous solution of the potassium derivative of ethyl oxalacetate (1 mol.), cooled in a freezing mixture. A sticky, red mass separated, from which, by crystallisation from alcohol, ethyl diketosuccinate *o*-tolylhydrazone was obtained, identical with that prepared by direct esterification.

Diketosuccinic acid o-tolyllosazone (V) was prepared by adding a solution of 26 g. of sodium dihydroxytartrate (1 mol.) in 180 c.c. of moderately concentrated hydrochloric acid (1:1) to a solution of 32 g. of *o*-tolylhydrazine (2 mols.) in 1500 c.c. of dilute hydrochloric acid (1:100). The mixture was stirred for 6 hours and heated at 80° for 2 hours. The *osazone* was filtered off without previous cooling, repeatedly washed with boiling water, and dried at 110° . It was thus obtained as an orange powder, m. p. 170° (decomp.) (Found: N, 15.6. $C_{18}H_{18}O_4N_4$ requires N, 15.8%).

Anhydrodiketosuccinic Acid o-Tolyllosazone (VI).—The *osazone* (V) was added to boiling acetic anhydride until no more would dissolve. On cooling, the *anhydride* separated in long, glistening, red prisms, m. p. 198° (decomp.) (Found: N, 16.6. $C_{18}H_{16}O_3N_4$ requires N, 16.7%).

4:5-Diketo-1-*o*-tolylpyrazoline-3-carboxylic acid 4-*o*-tolylhydrazone (VII) is formed together with the isomeric anhydride (VI) on crystallising the *osazone* (V) from acetic acid. It is, however,

best obtained by acidifying the orange-coloured solution produced by dissolving the osazone in hot 10% sodium hydroxide solution; the *tolylyhdrazone* thus obtained separates from acetic acid, in which it is sparingly soluble, in very small, yellow prisms, m. p. 229° (decomp.) (Found : N, 16.45. $C_{18}H_{16}O_3N_4$ requires N, 16.7%).

Its *ethyl* ester (VIII), obtained by boiling the osazone (V), the anhydride (VI), or the pyrazolone (VII) with alcohol containing 5% of dry hydrogen chloride, crystallises from alcohol, in which it is easily soluble, in long, orange-red prisms, m. p. 145° (Found : N, 15.5. $C_{20}H_{20}O_3N_4$ requires N, 15.4%).

The following derivatives of *p*-tolylyhydrazine were similarly prepared.

Diketosuccinic acid p-tolylyhdrazone (I) is moderately easily soluble in 75% acetic acid, from which it separates in orange-yellow octahedra, m. p. 190° (decomp.) (Found : N, 11.3%). The *anhydride* (II) crystallises from acetic anhydride in deep red, elongated prisms, m. p. 192° (decomp.) (Found : N, 12.1%). The *half-ester* (III) is easily soluble in alcohol, from which it separates in lemon-yellow, slender prisms, m. p. 112° (Found : N, 10.05%).

Diketosuccinic acid p-tolylosazone (V) was obtained as a soft, orange-red powder, m. p. 175° (decomp.) (Found : N, 15.65%). The *anhydride* (VI) forms red, elongated prisms, m. p. 230° (decomp.) (Found : N, 16.5%).

4 : 5-Diketo-1-p-tolylypyrazoline-3-carboxylic acid 4-p-tolylyhdrazone (VII) is sparingly soluble in acetic acid, from which it separates in very small, pale yellow prisms, m. p. 233° (decomp.) (Found : N, 16.7%). Its *ethyl* ester (VIII) is easily soluble in alcohol, from which it separates in orange-red, slender prisms, m. p. 143° (Found : N, 15.55%).