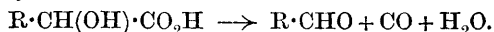


CXXVI.—*The Action of Heat on α -Hydroxycarboxylic Acids. Part III. $\alpha\alpha'$ -Dihydroxysebacic Acid and its Diacetyl Derivative.*

By HENRY RONDEL LE SUEUR.

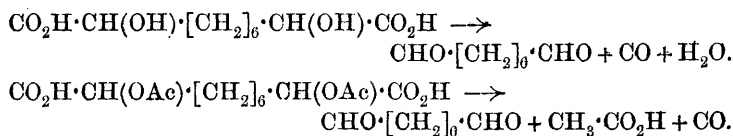
THE previous communications (Trans., 1904, 85, 827 ; 1905, 87, 1888) relating to this investigation dealt with the α -monohydroxy-derivatives of monocarboxylic acids, and it was shown that when these acids are heated at 270° they decompose with evolution of carbon monoxide and formation of aldehydes containing one atom of carbon less than the parent hydroxy-acids



The present communication deals with a similar investigation of the

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action of heat on $\alpha\alpha'$ -dihydroxysebacic acid and its diacetyl derivative, and the results now brought forward show that these compounds when heated undergo a decomposition similar to that of the monohydroxy-derivatives of the monobasic acids:



In this case the aldehyde produced is suberic dialdehyde, a substance which has been obtained previously by Baeyer (*Ber.*, 1897, 30, 1962) by the oxidation of the barium salt of dihydroxysebacic acid by means of lead dioxide and phosphoric acid. Baeyer showed that this dialdehyde is a liquid which very readily polymerises, and that even after the short interval of half an hour the substance has polymerised to a caoutchouc-like mass.

The present author was unable to obtain the aldehyde in a pure state, a want of success which in his opinion is to be ascribed to the unstable nature of the aldehyde rather than to the inapplicability of this method to the α -hydroxy-derivatives of dibasic acids in general.

That suberic dialdehyde is produced by heating $\alpha\alpha$ -dihydroxysebacic acid or its diacetyl derivative is proved conclusively by the fact that the product obtained polymerised as described by Baeyer, that it formed a crystalline compound with sodium hydrogen sulphite, and when oxidised with potassium permanganate gave suberic acid; further, it formed an oxime which melted at the same temperature as the oxime of suberic dialdehyde.

It was intended to include in this communication the investigation of the action of heat on α -monohydroxysebacic acid, which it was hoped to obtain by the hydrolysis of the corresponding α -monobromo-derivative. Unfortunately all attempts to prepare this bromo-derivative have failed up to the present, and in all cases where this substance might be expected to be produced only the dibromo-derivative or unbrominated sebacic acid was obtained, and there was no satisfactory evidence of the formation of the monobromo-derivative.

The following is a very brief summary of some of the experiments made in this direction:

(a) Bromination of sebacic acid with amorphous phosphorus and bromine, using only sufficient bromine to form the monobromo-derivative of the acid dibromide.

(b) Conversion of the sebacic acid (1 mol.) into its acid chloride by means of phosphorus pentachloride, and acting on the resulting compound with bromine (1 mol.).

(c) The interaction of equimolecular proportions of bromine and the mono-acid chloride of the monoethyl ester of sebacic acid.

EXPERIMENTAL.

Preparation of $\alpha\alpha'$ -Dibromosebacic Acid.

Forty grams of dry bromine were gradually added to an intimate mixture of 1.5 grams of dry amorphous phosphorus and 12 grams of sebacic acid (m. p. $130-131^\circ$), and the whole heated on the water-bath for five hours, at the end of which time the whole of the free bromine had disappeared. The resulting bromo-acid bromide was gradually poured into 40 c.c. of formic acid (sp. gr. 1.22) and the whole heated on the water-bath for half an hour. The dibromo-acid which separated after cooling was filtered and recrystallised, first from formic acid and then finally from chloroform until its melting point was constant:

0.2554 gave 0.2663 AgBr. Br = 44.36.

$C_{10}H_{16}O_4Br_2$ requires Br = 44.44 per cent.

$\alpha\alpha'$ -Dibromosebacic acid crystallises in long needles melting at $117-120^\circ$. The melting point found for this substance by Auwers and Bernhardt (*Ber.*, 1891, **24**, 2232) is $117.5-119^\circ$, whereas Weger (*Ber.*, 1894, **27**, 1212) states that it melts at 136° , and Claus and Steinkauler (*Ber.*, 1887, **20**, 2883) quote 115° as the melting point of the pure substance.

Preparation of $\alpha\alpha'$ -Dihydroxysebacic Acid.

Ten grams of the pure $\alpha\alpha'$ -dibromosebacic acid were neutralised with 50 c.c. of an aqueous solution of sodium hydroxide and the solution of the sodium salt boiled for one and a half hours. The resulting strongly acid solution was again neutralised with sodium hydroxide and boiled for another hour, and this process repeated until the solution no longer became acid after boiling for a period of one hour. The resulting dihydroxy-acid was converted into the insoluble zinc salt, which, after being washed free from sodium bromide, was decomposed with hydrogen sulphide. The aqueous solution of the free acid was filtered from the zinc sulphide, evaporated to dryness, and the acid recrystallised from a mixture of ethyl acetate and chloroform, when it melted at $125-127^\circ$:

0.1534 gave 0.2888 CO_2 and 0.1088 H_2O . C = 51.34; H = 7.88.

$C_{10}H_{18}O_6$ requires C = 51.28; H = 7.69 per cent.

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Claus and Steinkauler (*loc. cit.*, 2888) quote 130° as the melting point of this acid, whereas Weber (*loc. cit.*, 1215) states that it melts at 124°.

Action of Heat on $\alpha\alpha'$ -Dihydroxysebacic Acid.

The pure dihydroxysebacic acid was heated in a distillation flask attached to a condenser; when the temperature reached 230° the substance frothed a good deal, carbon monoxide was evolved, and a small quantity of liquid distilled over. As the temperature rose, the mass gradually turned yellow and showed signs of charring, and although the temperature was raised to above 300°, very little more liquid distilled. The small quantity of distillate which was obtained had a characteristic odour of α -nthaldehyde, readily reduced potassium permanganate, and formed a semicarbazone melting at 176—181° and decomposing with evolution of gas at 184°.

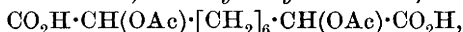
Baeyer (*Ber.*, 1897, 30, 1964) states that the semicarbazone of suberic dialdehyde melts and evolves gas at 183—185°.

The above experiment shows that suberic dialdehyde is formed when $\alpha\alpha'$ -dihydroxysebacic acid is heated, but as the yield was very small, it was decided to try the action of heat on the diacetyl derivative of the acid, and this experiment was attended with more satisfactory results.

Action of Heat on the Diacetyl Derivative of $\alpha\alpha'$ -Dihydroxysebacic Acid.

Preparation of the Diacetyl Derivative.—Forty grams of dihydroxysebacic acid, 80 grams of fused sodium acetate, and 320 grams of acetic anhydride were mixed together in a flask attached to a reflux condenser, and the mixture boiled for five and a half hours. The excess of acetic anhydride was removed by distillation in a vacuum and the residue dissolved in water; on the addition of an excess of dilute sulphuric acid to this solution, the acetyl derivative was precipitated as an oil, which was extracted with ether, and the ethereal solution washed, dried, and evaporated.

The *diacetyl derivative of $\alpha\alpha'$ -dihydroxysebacic acid*,



is a thick oil which is insoluble in water and does not solidify on keeping for a long time or on cooling to a low temperature; as it cannot be distilled even in a vacuum without decomposition, it was not further purified.

Fifty grams of the diacetyl derivative were heated in a distillation flask attached to a condenser and provided with a thermometer which dipped into the substance. When the temperature reached 210° a colourless liquid, chiefly acetic acid, distilled over; at 230° the mass frothed and carbon monoxide was evolved, and at 250° the evolution

of gas was rapid, and an oily, yellow liquid passed over. When the temperature reached 300° the heating was discontinued as the evolution of carbon monoxide had practically ceased, and there was evidence of a secondary decomposition. The residue left in the flask was of a very spongy nature, and weighed 5 grams. The carbon monoxide was collected, and its volume corresponded approximately with that required by theory; it contained a small percentage of carbon dioxide. The distillate obtained from the heating of three quantities of 50 grams each was dried over anhydrous sodium sulphate and then distilled in air until the temperature had reached 140° , when the distillation was continued in a vacuum. After repeated distillation, a fraction boiling at 143 — 148° , under 33 mm. pressure, was obtained, which had the characteristic properties of the dialdehyde of suberic acid. It had a characteristic odour of α -nthaldehyde, polymerised to a semi-transparent yellow solid, formed a crystalline compound with sodium hydrogen sulphite, and readily reduced potassium permanganate in the cold.

A portion of the above fraction was dissolved in acetone and finely powdered potassium permanganate added until no further reduction took place on heating. The residue left after evaporation of the acetone was diluted with water and acidified with dilute sulphuric acid, and the manganese dioxide dissolved by means of sulphurous acid. The resulting liquid was repeatedly extracted with ether, and the residue left on evaporation of the ethereal solution was crystallised first from ether and lastly from water, when it melted at 139 — 140° , which is the melting point of suberic acid. It was analysed with the following result:

0.1476 gave 0.2972 CO_2 and 0.1096 H_2O . $\text{C} = 54.91$; $\text{H} = 8.25$.

$\text{C}_8\text{H}_{14}\text{O}_4$ requires $\text{C} = 55.17$; $\text{H} = 8.05$ per cent.

Another portion of the same fraction was treated with hydroxylamine hydrochloride and sodium acetate in the usual way, and the oxime, which separated after some time, was recrystallised from absolute alcohol, when it melted at 151 — 152° , a melting point which agrees with that given by Baeyer (*loc. cit.*) for the dioxime of suberic dialdehyde, namely, 150 — 155° . On analysis:

0.1222 gave 16.7 c.c. moist nitrogen at 16° and 764 mm. $\text{N} = 16.02$.

$\text{C}_8\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{N} = 16.27$ per cent.

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