

XXII.—On Nitrobenzalmalonic Acids.

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IN a former communication (Trans., 1883, p. 409), I mentioned that I had obtained an acid by the condensation of orthonitrobenzaldehyde with malonic acid, and at that time I believed it was not an unsaturated acid. The following account will show that the statement requires correction.

In order to prepare the acid, a mixture of orthonitrobenzaldehyde with sodium malonate and glacial acetic acid is allowed to remain for a few days at the ordinary temperature; it is then treated with water, and the excess of aldehyde removed by means of ether; after the addition of hydrochloric acid to the aqueous solution, the new acid may be dissolved out by agitation with ether. It may, however, be prepared more expeditiously as follows:—

A mixture of glacial acetic acid, malonic acid, and orthonitrobenzaldehyde is warmed for eight hours at 60° , water is then added, and any precipitate of unchanged orthonitrobenzaldehyde is filtered off. The aqueous solution is extracted with ether, and the residue left on distilling off the ether is evaporated with water on the water-bath, to remove acetic acid. The impure acid thus obtained may be purified as follows:—It is dissolved in ether, and carbon bisulphide added till the colouring matter, but not the acid, is precipitated; it is then filtered, and more bisulphide is added to the clear solution, when the acid crystallises out well; it still contains a trace of malonic acid, but this may be removed by recrystallising it from water, from which it separates in needles.

Of a specimen submitted to analysis—

0·3578 gram gave 0·0992 gram H_2O and 0·6647 gram CO_2 .

0·5016 „ 26 c.c. nitrogen at $14^{\circ} C.$, and 762 mm. pressure.

	Found.	Theory for $C_{10}H_7NO_6$.
C.....	50·66	50·65
H	3·08	2·95
N	6·10	5·90

The silver salt was also prepared by neutralising a solution of the acid with ammonia, and precipitating with silver nitrate. On analysis—

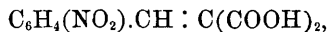
0.5938 gram gave 0.5877 gram CO_2 and 0.0721 gram H_2O .

0.4202 „ 0.2641 „ AgCl .

0.3267 „ 0.2066 „ „

	Theory for $\text{C}_{10}\text{H}_5\text{NO}_6\text{Ag}_2$.	Found.	
		I.	II.
C	26.60	26.99	—
H	1.10	1.34	—
Ag	47.89	47.35	47.59

The acid is therefore orthonitrobenzalmalonic acid,



and is isomeric with the paranitrobenzalmalonic acid described in my previous paper. It melts at 161° with evolution of carbonic anhydride and carbonisation; it dissolves readily in water, is very soluble in ether, sparingly in chloroform, and insoluble in benzene and carbon bisulphide; it gives a red colour when warmed with concentrated sulphuric acid.

Barium Salt.—If a solution of the acid is neutralised with ammonia, and barium chloride is added, a very beautiful salt is deposited in white feathery tufts; this salt, however, cannot be recrystallised, as when it is warmed with water, it is at once converted into another salt, consisting of small hard insoluble nodules.

Of the feathery tufts submitted to analysis—

0.2147 gram lost at 120° 0.234 gram, and gave 0.1187 gram barium sulphate.

	Theory for $\text{C}_{10}\text{H}_5\text{NO}_6\text{Ba}, 2\frac{1}{2}\text{H}_2\text{O}$.	Found.
H_2O	10.79	10.89
Ba	32.85	32.50
Calculated for dry salt.		Found.
Ba	36.81	36.48

Of the hard nodules submitted to analysis—

0.5208 gram dried at 130° gave 0.3096 gram BaSO_4 .

0.681 „ „ 160° „ 0.4083 „ „

	Theory for $\text{C}_{10}\text{H}_5\text{O}_6\text{Ba}, \text{H}_2\text{O}$.	Found.	
		I.	II.
Ba	35.12	34.95	35.26

As the acid obtained from these two salts was the same, they are obviously two barium salts of orthonitrobenzalmalonic acid, containing different amounts of water of crystallisation; that of the latter is not given up at 160° .

The chief point of interest about this acid is its remarkable stability; whilst benzalmalonic acid, its paranitro-derivative, and, as we shall see later, its metanitro-derivative, are decomposed by boiling with water, orthonitrobenzalmalonic acid can be boiled for any length of time with dilute acids, without undergoing the slightest decomposition. I had indeed expected that the presence of the nitro-group in the ortho-position would increase the stability to such an extent as to enable me to extract a hydroxy-acid of the composition



in accordance with Baeyer and Einhorn's results quoted in my previous paper. The results show that although the stability is very materially increased by the presence of the nitro-group, yet no hydroxy-acid is obtained.

Having thus obtained and compared benzalmalonic acid with its ortho- and para-nitro-derivatives, it appeared to be of interest to prepare the metanitro-derivative, and observe its properties.

Equal weights of metanitrobenzaldehyde and malonic acid were heated with glacial acetic acid at 60° ; in a few hours the mixture became almost solid from the formation of crystals; these were drained from acetic acid by a filter-pump, recrystallised from hot water, and washed with chloroform to remove metanitrobenzaldehyde.

Of a specimen submitted to analysis—

0.4067 gram gave 0.7576 gram CO_2 , and 0.1127 gram H_2O .

	Theory.	Found.
C.....	50.65	50.79
H	2.95	3.07

It is therefore metanitrobenzalmalonic acid. It melts at 205° with evolution of carbonic anhydride, leaving a residue of metanitrocinnamic acid melting at 196° .

It dissolves readily in hot water, being at the same time partially decomposed into metanitrobenzaldehyde, which accompanies the acid as it crystallises, and malonic acid, which can be extracted from the mother-liquors; it is only slightly soluble in cold water and ether; dissolved in ammonia, it gives precipitates of acicular crystals with solutions of barium and of calcium chloride.

I now wished to ascertain which of these acids would be produced by the direct nitration of benzalmalonic acid, but it was found that on adding benzalmalonic acid to fuming nitric acid cooled with ice,

rapid oxidation took place, with evolution of red fumes. On pouring the solution into water, paranitrobenzaldehyde and paranitrobenzoic acid, melting at 240° , were obtained. It was therefore resolved to nitrate the ethyl salt.

The ethyl salt, prepared by boiling benzalmalonic acid with alcohol and strong sulphuric acid, was distilled in a vacuum. The properties of this salt have been described by Claisen (*Ber.*, **14**, 348; and *Annalen*, **218**, 129). It was added to fuming nitric acid, cooled with a mixture of ice and hydrochloric acid, and the solution poured into ice-cold water; a crystalline precipitate settled, which was washed with sodium carbonate and sodium hydrogen sulphite solutions, and crystallised from alcohol.

The first crop of crystals consisted of fine long prisms, melting at 93° .

On analysis—

0.4166 gram gave 0.1824 gram H_2O , and 0.8758 gram CO_2 .

0.351 ,, 15.2 c.c. N at 13° and 748 mm. pressure.

	Found.	Theory.
C.	57.33	57.33
H	4.86	5.11
N	5.02	4.77

On saponification, by boiling with a mixture of equal parts of glacial acetic acid, strong sulphuric acid, and water, paranitrobenzalmalonic acid (melting at 227° with evolution of carbonic anhydride) was obtained.

The second crop of crystals consisted of rhombs, which after recrystallisation melted at 53° , and upon saponification in the same way, give the orthonitrobenzalmalonic acid described above.

On analysis—

0.3778 gram gave 0.7897 gram CO_2 , and 0.1726 gram H_2O .

0.2705 ,, 11.8 c.c. at 13° and 739 mm. pressure.

	Found.	Theory.
C.	57.00	57.33
H	5.07	5.11
N	5.00	4.77

From 11 grams of ethyl salt, 6.3 grams of the para- and 2.8 grams of the ortho-nitro-salt were obtained, being 48 and 21 per cent. of theory respectively. This is worthy of notice, because ethyl cinnamate on nitration gives 40 per cent. of the para- and 60 per cent. of the ortho-nitro-compound; whereas ethyl benzalmalonate, nitrated by acid cooled only with ice, gives but a trace of the orthonitro-derivative,

and when the acid is cooled by a freezing mixture the ortho-compound is produced in the small proportion mentioned above.

I am proceeding to investigate the additive compounds of these acids, which seem to promise something of interest.
