THE SUBSTITUTION OF HYDROGEN FOR CHLORINE IN TRICHLORMETHYLPARACONIC ACID.

(SECOND PAPER.)

BY HENRY C. MYERS.

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IN the *Journal of the Chemical Society* for June, 1897, I called attention to some extremely unstable condensation products resulting from the reduction of dichlormethylparaconic acid in attempting to eliminate the remaining chlorine atoms. One compound being monochlordiparaconic acid, $C_9H_9ClO_2$, and another, also an acid, having the formula $C_9H_{12}O_2$. Secondary to other published work, I have continued these investigations.

Finding that the reduction of the dichlor acid by various agents was not in the direction of methylparaconic acid, which substance I hoped to reach by this method, I decided to treat the trichlor acid with sodium amalgam, the trichlor acid being readily prepared on condensation of chloral with sodium succinate in the presence of a suitable dehydrating agent.[1]

Trichlormethylparaconic acid was dissolved in water, treated with sodium hydroxide to retard the action of free acid, small pieces of solid sodium amalgam added occasionally and the cylinder surrounded with ice. Frequently during a two-days' treatment, sulphuric acid was added to prevent the solution becoming more than weakly alkaline. Eventually sulphuric acid was added in large excess and the mixture extracted with ether; on recrystallization from water the result was found to be an almost quantitative yield of the dichlor acid. This method, as regards the preparation of dichlormethylparaconic acid, is much simpler than the laborious process of reducing with zinc dust and acetic acid and finally precipitating with hydrogen sulphide as described by Miller (*Loc. cit.*), large amounts of zinc being precipitated completely only on repeated treatment with hydrogen sulphide, and filtration being extremely slow and unsatisfactory.

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[1] Miller: *Ber. d. chem. Ges.*, **23**, R. 92 (1890); *Ann. Chem.* (Liebig), **255**, 43.

LONG-CONTINUED REDUCTION.

The above treatment with sodium amalgam when continued for a week or ten days resulted in three definite compounds, one of which has never been previously observed; (*a*) the dichlor acid with its characteristic properties and melting-point of 142°; (*b*) monochlordiparaconic acid of orange color and melting-point of 220°, obtained by recrystallization from alcohol; (*c*) a new acid in relatively small amounts with melting-point of 126°-127° and found in the final ether extraction as follows: On completion of the treatment with sodium amalgam the solution was acidified with hydrochloric acid. The monochlordiparaconic acid being insoluble in water formed an extremely voluminous precipitate which was filtered off and recrystallized from alcohol. The filtrate on extraction with ether yields the white crystalline dichlor acid, readily purified by crystallization from water. Repeated extraction with ether gives a yellowish oil which on long standing over sulphuric acid forms well defined crystals. These on being recrystallized from water and washed with ether have a constant melting-point of 126°-127°, resemble benzoic acid in appearance, do not decompose on standing for a year, are soluble in sodium carbonate solution, acid to litmus, and do not decompose on repeated melting.

BEHAVIOR OF MONOCHLORDIPARACONIC ACID TOWARDS HEAT.

In making melting-point determinations of this acid in the usual way, with capillary tube and paraffin-bath, it was noticed that the acid on melting underwent decomposition giving off a gas in small bubbles. In order to observe the change more closely, a long slender test-tube was substituted and considerable material used. In this way it could be observed that the substance really began its decomposition at about 190°, giving off fumes of hydrochloric acid and depositing white needle-like crystals on the tube just above the paraffin. I doubt if the true conditions of melting-points so called, can be observed in minute capillary tubes. These observations resulted in my placing about 3 grams of material in a U-tube heating the same as high as 226°, meanwhile drawing air through the apparatus. The air was previously freed of moisture and carbon dioxide; the products of the change were drawn through calcium chloride, silver nitrate and caustic potash. Sublimation began at 181° followed by an effervescence of gas at 190°. The following figures show the total loss in weight in the U-tube and the corresponding increase in weight in each of the receiving tubes:

	Gram.
Loss in U-tube	0.6097
Gain in calcium chloride tube	0.0369
Gain in caustic potash tube	0.0662
Gain in silver nitrate tube	0.4854

CALCULATED LOSS CORRESPONDING TO 1 MOLECULE OF EACH GAS USING 2.9470 GRAMS OF MATERIAL.

	Calculated.	Found.
Hydrochloric acid gas	0.5830	0.4854
Water	0.2875	0.0369
Carbon dioxide	0.7028	0.0662
		0.5885

As the weights of water and carbon dioxide are too low for the loss of a single molecule and the total gain corresponds almost exactly with the loss of a single molecule of hydrochloric acid (calculated 0.5830, found 0.5885) I assume that the change is represented by the following reaction:

$$C_9H_9ClO_2 = HCl + C_9H_8O_2,$$

and that the increase in weight in the calcium chloride and caustic potash tubes were due to hydrochloric acid alone.

CONCLUSION.

Trichlormethylparaconic acid on reduction with either zinc dust or sodium amalgam in the presence of acids produces the dichlor acid in almost quantitative amounts, except where treatment is long continued with the amalgam. In the latter case, three distinct and well defined acids result; *viz.*, Dichlormethylparaconic acid, monochlordiparaconic acid, and a new acid with melting-point at 126°-127°. The dichlor acid on reduction produces monochlordiparaconic acid, according to the following equation:[1]

$$2C_6H_6O_4Cl_2 = C_9H_9O_2Cl + 3HCl + 3CO_2.$$

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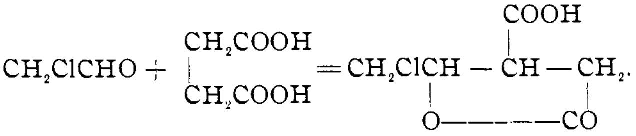
[1] *J. Chem. Soc.*, June, 1897.

Monochlordiparaconic acid on reduction forms an acid, $C_9H_{12}O_2$, which I found too unstable for investigation. Considering that these reductions do not lead in the direction of methylparaconic acid and that aldehyde as well as chloral condenses with sodium succinate in the presence of dehydrating agents, it would be of interest to treat similarly the monochlor aldehyde. Possibly the following change might result:



$$CH_2ClCHO + \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array} = \begin{array}{ccccc} & & COOH & & \\ & & | & & \\ CH_2ClCH & - & CH & - & CH_2. \\ | & & & & | \\ O & - & - & - & CO \end{array}$$

This monochlormethylparaconic acid, which I believe has never been prepared, might reduce to methylparaconic acid and yet the tendency of these compounds seems to be to double the molecular weight on giving up chlorine. On account of the extreme complexity of these changes and the instability of resulting compounds, as well as the great length of time necessary to prepare material, very little progress can be made unless one is willing to devote a year to the queston as it now stands.

UNIVERSITY OF CALIFORNIA.

[CONTRIBUTION FROM THE NORTH CAROLINA EXPERIMENT STATION.]

NITRIFICATION IN DIFFERENT SOILS.[1]

BY W. A. WITHERS AND G. S. FRAPS.

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IN a previous article[2] the authors communicated some work on the rate of nitrification of some fertilizers in a pasture soil, in which it was found that the percentages of nitrogen in them nitrified in a definite time corresponded with their availability as measured by vegetation tests, with one exception. This exception was ammonium sulphate, which was nitrified to a very small extent, although it has a high availability.

Inasmuch as the prevailing opinion in regard to the process of nitrification is that organic nitrogen is first converted into am-

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[1] An account of this work was read before the Association of Official Agricultural Chemists in November, 1901.

[2] This Journal, **23**, 318 (1901).