TABLE I

ANALYTICAL AND OTHER DATA OF THE ACIDS

β-( )-β-( )-amino-propionic acids	Yield, g.	Yield, %	M. p., °C.	Formula	Analysis, N, % Calcd.	Analysis, N, % Found
Piperonyl, ethyl	9.4	26	198–200	$C_{12}H_{15}O_4N$	5.90	5.60
Piperonyl, dimethyl-[a]	1	2–3	.....	$C_{12}H_{16}O_4NCl$[a]	5.12	5.32
β-( )-β-( )-ethane-α,α-dicarbonic acids						
Phenyl, amino	30.0	76	148	$C_{10}H_{11}O_4N$	6.69	6.98
Phenyl, piperidyl	11.8	91	163–164[b]	$C_{15}H_{19}O_4N$	5.05	5.07
Piperonyl, piperidyl	8	87	150–152[b]	$C_{15}H_{19}O_6N$	4.36	4.42
Phenyl, ethylamino	6	68.8	163–164[b]	$C_{12}H_{15}O_4N$	5.9	6.54
Piperonyl, ethylamino	5.8	58.2	155–157[b]	$C_{13}H_{15}O_6N$	4.98	4.94

[a] Hydrochloride. Calcd.: Cl, 12.95. Found: 13.09.

[b] With decomposition.

β-Piperonyl-β-ethylamino-ethane-α,α-dicarbonic Acid (Z.), $CH_2O_2C_6H_3CH(NHC_2H_5)CH(COOH)_2$.—Five and three-tenths g. of piperonal, 3.85 g. of malonic acid and 12 cc. of 15% alcoholic ethylamine solution were mixed and treated as in the previous experiment. The acid is easily soluble in hot water, less so in alcohol and insoluble in ether; it crystallizes from alcohol in little rods.

Summary

A new explanation of the mechanism of Knoevenagel's synthesis of cinnamic acids is proposed, a method of preparation of aryl-β-amino-ethanedicarbonic acids and their N-substituted derivatives is described and the specific preparation of some compounds of this type and the properties of these compounds are given.

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[CONTRIBUTION FROM THE FAYERWEATHER CHEMICAL LABORATORY OF AMHERST COLLEGE]

REACTION OF CHLORO-ACETIC ACIDS WITH ZINC

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RECEIVED OCTOBER 13, 1928 PUBLISHED MARCH 6, 1929

In previous contributions from this Laboratory[1,2] the reaction of trichloro-acetic acid with copper has been discussed and it has been shown that it affords an excellent method for the preparation of dichloro-acetic acid. The reaction is exothermic and the acid was used in benzene solution. During these investigations it was noted that the reaction of trichloro-acetic acid with zinc is also very vigorous, and the present authors, therefore, have studied this reaction. The work has been interrupted by change of residence of the junior author, so it seems advisable to make a brief statement of results so far obtained.

When zinc dust is added to a solution of trichloro-acetic acid in benzene,

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[1] Doughty and Freeman, THIS JOURNAL, **44**, 636 (1922).

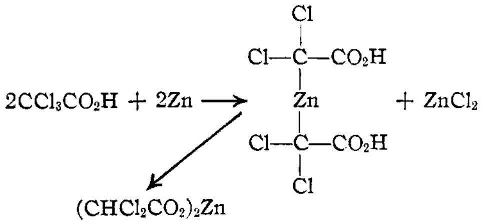
[2] Doughty and Black, *ibid.*, **47**, 1091 (1925).

much heat is evolved and zinc chloride is formed, together with zinc dichloro-acetate and other products, depending on the relative quantities of acid and zinc. The reaction product is not easy to work with, owing apparently to the hygrosopic nature of the zinc chloride; the reaction was therefore studied in aqueous solution and it was found that it is not necessary to use zinc dust, as mossy zinc reacts very readily.

The least expected of the results obtained in these experiments is the fact that no hydrogen is evolved. When one mole of trichloro-acetic acid, dissolved in one liter of water, reacts with one gram atomic weight of mossy zinc, the zinc is dissolved very rapidly, the solution becomes neutral and contains zinc chloride and zinc dichloro-acetate, but no hydrogen is evolved. If more than this amount of mossy zinc is added the excess remains after the reaction is over. If zinc dust is added in excess, however, a white precipitate forms and part of the zinc dust is converted into zinc chloride. This white precipitate has not been identified. It contains zinc and is soluble in acids. The reaction of trichloro-acetic acid with mossy zinc is quantitative and the equation is

$$2CCl_3CO_2H + 2Zn = ZnCl_2 + (CHCl_2CO_2)_2Zn$$

The fact that no hydrogen is evolved in this reaction indicates that the mechanism of the reaction must be considered as similar to that of trichloro-acetic acid with copper. It has been suggested[1,2] that with copper an intermediate compound is formed in which the copper is joined directly to the carbon and that this is followed by a rearrangement in which hydrogen and copper exchange places. A similar mechanism for the reaction of trichloro-acetic acid with zinc would be expressed by the following



$$2CCl_3CO_2H + 2Zn \longrightarrow \begin{array}{c} Cl \\ | \\ Cl{-}C{-}CO_2H \\ | \\ Zn \\ | \\ Cl{-}C{-}CO_2H \\ | \\ Cl \end{array} + ZnCl_2 \longrightarrow (CHCl_2CO_2)_2Zn$$

As in the corresponding reaction with copper, the hydrogen shifts from the labile or ionizable position in the carboxyl group to the very stable position in the dichloromethyl group. Apparently this reaction is very much more rapid than the more usual replacement of hydrogen ions by zinc ions as in the action of hydrochloric acid with zinc. The fact that a corresponding action takes place with copper and trichloro-acetic acid makes this explanation appear more probable than to assume that "nascent hydrogen" is formed which then reduces the trichloro-acetic acid to dichloro-acetic acid.

In a typical experiment, 32.8 g. (0.5 gram atomic weight) of "mossy" zinc was added to a solution of 81.7 g. (0.5 mole) of trichloro-acetic acid in 400 cc. of water and the mixture was stirred mechanically for three hours, when the zinc was completely dissolved and the solution was practically neutral, very slightly acid to litmus, but alkaline to methyl orange and lacmoid. In other experiments 10 g. of zinc in excess of the amount indicated by the equation brought the reaction to an end in one hour and a quarter, and the 10 g. of zinc remained.

The neutral solution resulting from the reaction was diluted to one liter and analyzed for chloride by the Mohr method and for zinc by titration with potassium ferrocyanide: calcd. for the equation given above: Cl, 0.500 gram atomic weight; Zn, 0.500 gram atomic weight. Found: Cl, 0.497; Zn, 0.480.

In another experiment, 53 g. of sodium carbonate (0.5 mole) was added to the neutral solution of zinc salts; the precipitated basic zinc carbonate was filtered off and the solution of sodium salts was evaporated to saturation and transferred to a distilling flask. An excess of concentrated sulfuric acid (75 cc.) was added and the mixture distilled at 25 mm. The fraction which distilled at 105° weighed 24 g. A portion of this distillate was dissolved in benzene and aniline was added. A white crystalline precipitate formed which, after recrystallizing, melted at 123–124°, which is the melting point of aniline dichloro-acetate. The product was further identified by a mixed melting point, using a sample of aniline dichloro-acetate prepared by the method of Doughty and Black.[2] Our acid boiled at 105° and 25 mm. Dichloro-acetic acid is reported[2] to boil at 102° and 20 mm.

In order to obtain some idea as to the energy of the reaction, which is strongly exothermic, 40.8 g. (0.25 mole) of trichloro-acetic acid was dissolved in 400 cc. of water in a thermos bottle which was provided with a one-holed rubber stopper through which passed a thermometer. "Mossy zinc," 16.4 g. (0.25 gram atomic weight) was added and the stopper with the thermometer was put in place. The bottle was shaken frequently and the time and temperatures were as follows.

Minutes	0	10	15	20	30	40	47	80
Temperature, °C	27	42	50	54	57	60	63	67

As in other cases, no hydrogen was evolved, and the solution was neutral (as defined above) at the end of the experiment, and all of the zinc was dissolved. The heat equivalent of the apparatus, as previously determined, was approximately 9.0 calories per degree. The specific heat of the substances present other than water is unknown, but an assumption of 0.25 seems reasonable. From these data we calculate the heat of the reaction as approximately 66,600 calories per mole of trichloro-acetic acid. Of this we can account for approximately 56,600 calories as the heat of formation of 0.5 mole of zinc chloride in solution, leaving approximately 10,000 calories per mole of trichloro-acetic acid for the other items involved in this reaction. No considerable accuracy is claimed for these figures, but they appear to us to have sufficient significance to justify us in mentioning the experiment.

The reaction in benzene is apparently the same as in water, and we have prepared aniline dichloro-acetate by this method also. There does not appear to be any advantage in this method of preparation of dichloro-acetic acid over that described by Doughty and Black.[2]

The corresponding reaction of dichloro-acetic acid with zinc is much less energetic. The amount of heat developed is not impressive, and it was necessary to heat, with stirring, for twelve hours on the water-bath to bring the solution to neutrality and to dissolve the zinc. There was some hydrogen evolved throughout the reaction and when the neutral solution was analyzed only 0.903 gram atomic weight of chlorine was found per mole of dichloro-acetic acid. Evidently in this case 90% of the reaction is similar to that of trichloro-acetic acid with zinc, while the other 10% takes the more usual course as when hydrochloric acid reacts with zinc.

The reaction of monochloro-acetic acid with mossy zinc is very slow, even on the water-bath or at boiling temperature. Time did not permit of a study of this reaction but it was noted that considerable hydrogen was evolved and the solution became neutral after about 100 hours. The analysis was not satisfactory, as apparently some acid was evaporated during the long period of heating. The solution also had some reducing effect on silver salts.

The marked difference in the speed of reaction of the chloro-acetic acids with zinc, and particularly the variation in the type of reaction as well, is interesting in connection with certain observations of one of us[3,4] concerning the reaction of compounds containing a trichloro- or tribromomethyl group with copper and with cuprous chloride in aqueous ammonia solution. It was shown that substances of this class (trihalogen methyl derivatives) are very much more reactive under the given conditions than those having fewer than three halogen atoms joined to one carbon atom.

Conclusion

When trichloro-acetic acid reacts with zinc in water solution, a neutral solution of zinc chloride and zinc dichloro-acetate is obtained. There is no evolution of hydrogen. The reaction is strongly exothermic.

With dichloro-acetic acid the corresponding reaction with zinc is much less exothermic, much slower and hydrogen is evolved to approximately 10% of the amount required by the equation $2HX + Zn = H_2 + ZnX_2$.

With monochloro-acetic acid the reaction is very slow and is to quite a large extent in accordance with the reaction just stated.

The reaction is similar to that in the case of trichloro-acetic acid and copper and an explanation of the mechanism is suggested.

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[3] Doughty, THIS JOURNAL, **39**, 2685 (1917).

[4] Doughty, *ibid.*, **41**, 1129 (1919).