

PLATE III.

Oliver W. Huntington, for the great aid he has given throughout this investigation. With the help of his skill in glass-blowing I have been able to secure all the connections of my gas generators with melted or cement joints, except the direct connections with the globe, where india-rubber could not be avoided. He has also constantly assisted my impaired eyesight in the observations with barometer and thermometer on which the accuracy of the work greatly depended. I have likewise been indebted to Dr. Arthur M. Comey for making the titrations required, and to Mr. W. W. Bosworth for the drawings with which this paper is illustrated.

XIX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

ON THE ACTION OF SODIUM MALONIC ESTER ON
TRIBROMDINITROBENZOL.

SECOND PAPER.

BY C. LORING JACKSON AND W. S. ROBINSON.

Presented May 28, 1889.

In a previous paper * on this subject we were obliged to publish several results in an unfinished condition, because at the time we saw no chance of being able to continue the work together. Since then, however, unforeseen circumstances have allowed us to go on with the research, and in this paper we describe work which fills up most of the gaps in our former publication.

The most important results contained in this paper may be stated briefly as follows. The reactions by which the bromdinitrophenylmalonic ester is formed have been made out to be the following: —

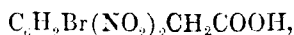
- I. $\text{C}_6\text{HBr}_2(\text{NO}_2)_2 + \text{CHNa}(\text{COOC}_2\text{H}_5)_2 =$
 $\text{NaBr} + \text{C}_6\text{HBr}_2(\text{NO}_2)_2\text{CH}(\text{COOC}_2\text{H}_5)_2.$
- II. $\text{C}_6\text{HBr}_2(\text{NO}_2)_2\text{CH}(\text{COOC}_2\text{H}_5)_2 + \text{CHNa}(\text{COOC}_2\text{H}_5)_2 =$
 $\text{C}_6\text{HBr}_2(\text{NO}_2)_2\text{CNa}(\text{COOC}_2\text{H}_5)_2 + \text{CH}_2(\text{COOC}_2\text{H}_5)_2.$
- III. $\text{C}_6\text{HBr}_2(\text{NO}_2)_2\text{CNa}(\text{COOC}_2\text{H}_5)_2 + \text{CH}_2(\text{COOC}_2\text{H}_5)_2 =$
 $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2\text{CNa}(\text{COOC}_2\text{H}_5)_2 + \text{CHBr}(\text{COOC}_2\text{H}_5)_2.$
- IV. $\text{CHNa}(\text{COOC}_2\text{H}_5)_2 + \text{H}_2\text{O} = \text{NaOH} + \text{CH}_2(\text{COOC}_2\text{H}_5)_2.$
- V. $\text{CHBr}(\text{COOC}_2\text{H}_5)_2 + \text{NaOH} = \text{NaBr} + \text{CHOH}(\text{COOC}_2\text{H}_5)_2.$

The proof of these reactions consisted in the isolation of tartronic acid from the mixture obtained by the saponification of the oily secondary product with hydrochloric acid.

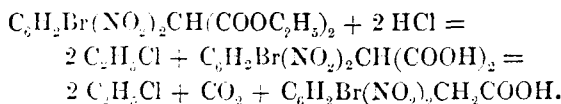
The action of concentrated hydrochloric acid, or, better, sulphuric acid of specific gravity 1.44, upon the bromdinitrophenylmalonic ester

* These Proceedings, xxiv. 1.

has been studied, and we are able to correct some of the preliminary statements made on this subject in our first paper. The product is the bromdinitrophenylacetic acid



which melts at 177° , and is formed, when hydrochloric acid is used, by the following reactions:—

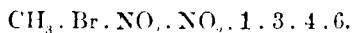


The crystalline silver salt of this acid was analyzed, and proved to have the formula



With sodic hydrate a deep Prussian green or with an excess a yellowish brown solution is formed, from which acids throw down a pale crimson precipitate, or a white one which becomes pale crimson when moistened with alcohol; none of these substances could be brought into a state fit for analysis, but we found that bromine was removed in their formation.

The bromdinitrophenylacetic acid is broken up when boiled with alcohol into bromdinitrotoluol and carbonic dioxide; boiling with water produces the same effect, but much more slowly. A few drops of sulphuric acid prevent the decomposition by boiling water. This conversion into bromdinitrotoluol gave us the means of determining the constitution of the bromdinitrophenylmalonic ester and its derivatives; as Messrs. W. B. Bentley and W. H. Warren have, at our request, worked out the constitution of the substituted toluol, and found that it is as follows:



It follows, therefore, that all the substances mentioned in this and our former paper must have a similar constitution, and that in making the bromdinitrophenylmalonic ester from bromdinitrobenzol the bromine atom replaced by the malonic radical is one of those which is at the same time para and ortho to the nitro groups, the one replaced by hydrogen is ortho to the two nitro groups, while the third atom of bromine, which remains unaltered, occupies exactly the same position as that replaced by the malonic ester radical, — certainly a curious result.

Preparation of Bromdinitrophenylmalonic Ester.

Our longer experience in the preparation of bromdinitrophenylmalonic ester has led us to introduce several improvements into the process, which now we carry on as follows. A strong benzol solution of 20 grs. of tribromdinitrobenzol (benzol is to be preferred to the ether used formerly, because the tribromdinitrobenzol is more soluble in it) is mixed with 16 grs. of malonic ester previously converted into sodium malonic ester by treatment with the sodic ethylate from 2.3 grs. of sodium and about 100 to 125 c.c. of alcohol, and the mixture allowed to stand over night at ordinary temperatures. The red solution thus obtained is treated with water, which separates it into two layers, a dark red aqueous solution containing the sodium salt of bromdinitrophenylmalonic ester and sodic bromide, and a benzol solution of the unaltered tribromdinitrobenzol with the oily product of the reaction. The two layers are separated with a drop-funnel, and the lower aqueous one acidified with dilute sulphuric acid; this throws down a yellowish white precipitate of the bromdinitrophenylmalonic ester, which is purified by crystallization from hot alcohol, until it shows the constant melting point 76° .

In this way 20 grs. of tribromdinitrobenzol gave 7.9 grs. of the bromdinitrophenylmalonic ester,* and 5.1 grs. of tribromdinitrobenzol were recovered from the benzol solution. Subtracting this from the 20 grs. there are left 14.9 grs. of tribromdinitrobenzol, which entered into the reaction, and should have given the same weight, 14.9 grs., of the product, so that the yield was 53 per cent of the theory, or about the same as that obtained by the process as given in our first paper, which calculated in the same way becomes 50 per cent.

In the course of some other experiments the curious observation was made that it is not necessary to use sodic ethylate to bring about the action of malonic ester on the tribromdinitrobenzol, as a little of the red salt of bromdinitrophenylmalonic ester was formed when *aqueous* sodic hydrate was added to a mixture of the two organic

* Dr. G. D. Moore, in his work with me on the action of sodium acetacetic ester on tribromdinitrobenzol, has found that a much better yield is obtained if the mixture is boiled for an hour under a return condenser. This observation was not made until the work described in this paper was finished and Mr. Robinson had left Cambridge, so that it was not convenient to try the experiment of boiling the solution of sodium malonic ester and tribromdinitrobenzol, nor did it seem very desirable to do so, as when we first took up the subject such an experiment was tried, and seemed to yield very unfavorable results. I propose, however, to repeat the experiment next year, if I return to the study of these compounds.

C. L. J.

substances. This recalls the observation of Victor Meyer,* that homologues can be obtained from benzyli cyanide by using the alkylhaloid with powdered solid sodic hydrate instead of sodic ethylate, or from desoxybenzoin by the use of an alcoholic solution of an alkaline hydrate.

Study of the Reactions by which the Bromdinitrophenylmalonic Ester is formed.

One of the most important points, which want of time prevented us from considering in our first paper, was the mechanism of the reactions by which the bromdinitrophenylmalonic ester was formed from the tribromdinitrobenzol, and accordingly this was one of the first points to which we turned our attention in taking up the subject again. The reaction consists essentially, as our analyses of the product showed, in the replacement of one of the bromine atoms in the tribromdinitrobenzol by the malonic ester radical $\text{CH}(\text{COOC}_2\text{H}_5)_2$, and of a second by hydrogen forming $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2\text{CH}(\text{COOC}_2\text{H}_5)_2$, and the obscure part of it is the manner in which this second atom of bromine is replaced by hydrogen. The first step toward clearing up this obscurity was obviously to make out whether this atom of bromine was eliminated in the form of some organic compound, or as sodic bromide, which was done by the following quantitative determinations of the amount of sodic bromide formed in the reaction.

I. 20 grs. of tribromdinitrobenzol were treated with the sodium malonic ester from 16 grs. of malonic ester in the way already described, and, after precipitating the bromdinitrophenylmalonic ester from the aqueous solution with dilute nitric acid, and filtering it out, the amount of sodic bromide was determined by precipitation of argentic bromide from an aliquot part of the filtrate, and calculating the amount in the entire solution. In this way the whole solution was found to yield 13.81 grs. of argentic bromide, corresponding to 5.88 grs. of bromine. The benzol solution on evaporation yielded 5.1 grs. of tribromdinitrobenzol, which had not taken part in the reaction, leaving 14.9 grs. which had acted, and which would yield 5.89 grs. of bromine, if two of the atoms of bromine had been removed from each molecule as sodic bromide.

II. 20 grs. of tribromdinitrobenzol gave under the same conditions 13.8 grs. of argentic bromide corresponding to 5.87 grs. of bromine, but only 4.9 grs. of tribromdinitrobenzol were recovered unaltered.

* Ber. d. ch. G. 1888, p. 1201.