

XXI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.THE REACTIONS OF SODIC ALCOHOLATES WITH
TRIBROMTRINITROBENZOL.*

SECOND PAPER.

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Presented June 15, 1892.

IN our first paper on this subject we described some experiments which led to the replacement of nitro groups in symmetrical tribromtrinitrobenzol by ethoxy or methoxy radicals. These observations seemed to us of special interest because the three nitro groups are in the meta position in this compound, and, so far as we were aware, no case was known in which a nitro group in this position to others had been removed from the benzol ring. In fact the so-called rule of Laubenheimer stated that a nitro group is replaced only when it is in the ortho position to another. Even with the halogens cases where a radical in the meta position exercises a loosening effect on another are very rare, the only one which occurs to us being the conversion of symmetrical tribrombenzol into dibromanisol by the action of sodic methylate.†

Soon after the appearance of our paper C. A. Lobry de Bruyn published an account ‡ of some experiments with symmetrical trinitrobenzol and sodic methylate from which he obtained dinitroanisol, thus again removing a nitro group in the meta position to others. At the same time in an interesting discussion § of the replacement of nitro groups in aromatic compounds he showed that Laubenheimer's rule must be abandoned, since para as well as ortho nitro

* The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by W. H. Warren.

† Blau, *Monatsh. f. Ch.*, VII. 630.

‡ *Rec. Trav. Ch. des Pays-Bas*, IX. 208.

§ *Ibid.*, IX. 210.

compounds are attacked by alcoholates and other reagents with the removal of nitro groups. This publication brought to our notice an earlier paper* by him, in which he states that by the action of alcoholic potassic cyanide on metadinitrobenzol one nitro group is replaced by the ethoxy (or methoxy) radical, but at the same time an atom of cyanogen is substituted for one atom of hydrogen, giving as the product $C_6H_3NO_2OC_2H_5CN$. This curious result seems to have more affinity with the additions of hydrocyanic acid to nitro-halogen benzols studied by v. Richter† than to simple substitution; but nevertheless we have here the replacement of a meta nitro group by another radical. As Lobry de Bruyn's later work was published almost simultaneously with ours (although a little later), and had grown out of his earlier researches, we felt that the study of substitutions of nitro groups in simple trinitro compounds should properly belong to him, and after a pleasant correspondence on the subject it has been agreed that he should follow out this line of work, while we confine ourselves, so far as the removal of nitro groups is concerned, to the completion of our study of tribromtrinitrobenzol.

At present, therefore, we know only three meta nitro compounds from which nitro groups have been removed, dinitrobenzol, symmetrical trinitrobenzol, and symmetrical tribromtrinitrobenzol.

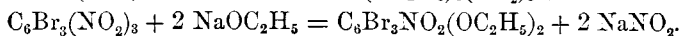
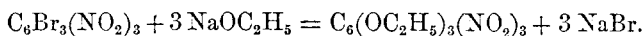
Lobry de Bruyn's work shows that the removal of nitro groups observed by us is caused by the position of these nitro groups, but the presence of the three meta bromine atoms evidently also has a loosening effect on the nitro groups, as we have replaced two of these groups by ethoxy radicals, whereas in the trinitrobenzol only one was replaced.

In taking up the study of the subject again, we first examined the action of tribromtrinitrobenzol and sodic ethylate more carefully, to see whether the bromine atoms were not also affected by it, and found that in addition to the tribromnitroresorcine diethylether there is always formed a quantity of trinitrophloroglucine triethylether, $C_6(OC_2H_5)_3(NO_2)_3$, melting at $119-120^\circ$; as however this substance is easily decomposed by sodic hydrate, the amount of it obtained as such is small, unless special precautions are taken to exclude atmospheric moisture. When such precautions are not taken, the trinitrophloroglucine triethylether is converted into the

* Rec. Trav. Ch., II. 205.

† Ber. d. ch. Ges., IV. 465, VII. 1145, VIII. 1418.

diethylether $C_6OH(OC_2H_5)_2(NO_2)_3$, melting at 89° , or trinitro-phloroglucine itself, $C_6(OH)_3(NO_2)_3$, (which melts at 167° instead of 158° , the point given by Benedikt,*) and these substances pass into the aqueous wash-waters as sodium salts. It follows therefore that the action of sodic ethylate on tribromtrinitrobenzol consists of the two following reactions, which take place parallel to each other:—



We observed further, that, if benzol and alcohol were used as the solvents instead of alcohol alone, more of the phloroglucine ether was obtained than when the solvent was only alcohol, and this led us to study the action quantitatively by determining the amounts of sodic nitrite and bromide formed, when we found that the amount of nitrite averaged with the benzol and alcohol 33.49 per cent; with alcohol alone, 45.92 per cent. There was also a difference in the reverse direction with the sodic bromide, but the percentages of this obtained under parallel conditions varied so materially that no careful comparison was possible. The percentages of sodic nitrite removed were, on the other hand, remarkably constant. We have not succeeded in finding any satisfactory explanation for this effect of the presence of benzol in promoting the formation of the trinitro-phloroglucine triethylether (produced by the first reaction), and diminishing the amount of tribromnitroresorcine diethylether formed by the second reaction given above.

We have also tried the action of several other alcoholates on tribromtrinitrobenzol, obtaining the following compounds:— $C_6Br_3NO_2(OCH_3)_2$, melting at 126° ; $C_6(OCH_3)_2OH(NO_2)_3$, melting at $77-78^\circ$; $C_6(OC_3H_7)_3(NO_2)_3$, from normal propyl alcohol, melting point $109-110^\circ$; the corresponding isocompound melting at 130° ; and $C_6(OCH_2C_6H_5)_3(NO_2)_3$, melting at 171° . A quantitative comparison of the amounts of sodic nitrite formed by different alcoholates indicated that the percentage removed diminishes as the molecular weight of the alcohol increases, but there were several exceptions to this general rule.

We have also found that sodic ethylate decomposes the triphenylether of trinitro-phloroglucine, converting it into the triethylether, while phenol is set free; and that sodic ethylate when heated with

* Ber. d. ch. Ges., XI. 1376.

the tribromnitroresorcine diethylether removes from it two atoms of bromine which are replaced by hydrogen, so that the product is bromnitroresorcine diethylether, $C_6H_2BrNO_2(OC_2H_5)_2$, melting at 115° ; — an observation which will be of value in discovering the cause of the strange replacements of bromine by hydrogen so often found in the course of this work.

PART I.

ACTION OF SODIC ETHYLATE ON TRIBROMTRINITROBENZOL.

In our earlier paper * on this subject we showed that sodic ethylate brought about a replacement of two of the nitro groups in tribromtrinitrobenzol by two ethoxy radicals forming tribromnitroresorcine diethylether, $C_6Br_3NO_2(OC_2H_5)_2$, as the principal product if alcohol was used as the only solvent and the mixture carefully cooled. There remained, however, several points which needed more careful examination, especially the effect upon the reaction of differences of temperature, the effect of using different solvents, and the source of the sodic bromide which was always formed in addition to the sodic nitrite. The results of our work on these subjects are given in the following paragraphs.

The experiments described in our first paper had led us to think that the tribromnitroresorcine diethylether was formed only when the mixture of tribromtrinitrobenzol and sodic ethylate was carefully cooled. To test the accuracy of this conclusion, we dissolved some tribromtrinitrobenzol in alcohol and a little benzol with the aid of heat, and added to the boiling solution in small quantities at a time enough sodic ethylate to give three molecules of the ethylate to each molecule of tribromtrinitrobenzol. As soon as all the ethylate had been added, the bright scarlet solution was allowed to cool, and then evaporated spontaneously. The aqueous washings of the residue gave a strong test for a nitrite, and also for a bromide. The portion insoluble in water was purified by crystallization from alcohol until it showed a melting point of 100° (the tribromnitroresorcine diethylether melts at 101°), when it was analyzed with the following result:—

0.2076 gr. of the substance gave by the method of Carius
0.2601 gr. of argentic bromide.

* These Proceedings, XXV. 183.

	Calculated for $C_6Br_3NO_2(OC_2H_5)_2$.	Found.
Bromine	53.57	53.32

This analysis with the melting point leaves no doubt that the substance is the expected tribromnitroresorcine diethylether, and therefore that the temperature of the reaction does not affect the nature of the principal product. We have accordingly omitted the cooling in our subsequent preparations of this body, simply allowing the mixture of tribromtrinitrobenzol, sodic ethylate, and alcohol to stand over night at ordinary temperatures.

The Modification of the Action when Benzol is used as one of the Solvents.

To study this subject the following experiment was tried. 10 gr. of tribromtrinitrobenzol were dissolved in dry benzol and an alcoholic solution of the sodic ethylate from 1.5 gr. of sodium added (these proportions are essentially three atoms of sodium to each molecule of tribromtrinitrobenzol). The first drop of the solution of sodic ethylate turned red as it was added, the color fading to yellow as the drop mixed with the liquid, so that, after all the ethylate had been added, the liquid had assumed an orange-red color. No evolution of heat was observed during the reaction. To make sure that the action was complete, the mixture was allowed to stand over night in a corked flask at ordinary temperatures, and then allowed to evaporate spontaneously, after which the residue was washed with water to remove the soluble salts.

Substances insoluble in Water. — The residue after washing with water was crystallized repeatedly from alcohol, and in this way a considerable quantity of the tribromnitroresorcine diethylether melting at 101° was obtained from the first crystals, while the mother liquors yielded a smaller quantity of another substance which when pure melted at $119-120^\circ$. This was dried at 100° , and analyzed with the following results: —

- I. 0.2159 gr. of the substance gave on combustion 0.3284 gr. of carbonic dioxide and 0.0914 gr. of water.
- II. 0.2080 gr. of the substance gave 22.5 c.c. of nitrogen at a temperature of 21° , and a pressure of 759.3 mm.

	Calculated for $C_6(OC_2H_5)_2(NO_2)_3$.	I.	Found.	II.
Carbon	41.75	41.49		
Hydrogen	4.35	4.70		
Nitrogen	12.17			12.30

It contained no bromine. There can be no doubt, therefore, that the product was the triethylether of trinitrophloroglucine, and that the formation of this substance produced the sodic bromide which was always obtained by the action of sodic ethylate on tribromtrinitrobenzol.

Properties of Trinitrophloroglucine Triethylether. — This substance crystallizes in long slender plates, terminated usually by one plane at a very sharp angle to the sides. These crystals are often united longitudinally into broader plates, which frequently have serrated ends, and may reach more than a centimeter in length and a millimeter in breadth. The color is white, but it turns brownish on exposure to the air. It melts at 119–120°; is soluble in cold ethyl or methyl alcohol, freely soluble in either of these solvents when hot; very freely soluble in benzol, chloroform, or acetone; freely soluble in glacial acetic acid; soluble in carbonic disulphide; slightly soluble in ligroine; essentially insoluble in water, whether cold or hot. The three strong acids have no perceptible action on it hot or cold, except that it is dissolved by hot strong nitric acid, but on dilution it is precipitated unchanged, to judge by the melting point. We have tried no experiments on its saponification by the long continued action of acids. A cold aqueous solution of sodic hydrate had no action upon it, and only a slight action when heated, but in alcoholic solution sodic hydrate decomposes it even in the cold, more rapidly when hot, forming a reddish yellow solution of the sodium salt of a phenol.

In addition to the tribromnitroresorcine diethylether and trinitrophloroglucine triethylether, we have always obtained from the crystallization a considerable amount of a substance which accumulated in the mother liquors and separated from its alcoholic solution as an oil solidifying after standing for some weeks. We have devoted a great deal of time to the study of this substance, because it appeared in such quantity that we thought it must be a principal product of our reaction; but this work has shown that it consists principally of the products already described, mixed with very little of an oily substance which prevents them from crystallizing as usual. In a preparation from 30 gr. of tribromtrinitrobenzol, the mother liquors gave 4.3 gr. of the more or less liquid fraction, but this amount was reduced to 1.2 gr. after removing the trinitrophloroglucine triethylether completely by treatment with alcoholic sodic hydrate, and the tribromnitroresorcine diethylether as nearly as possible by crystallization from alcohol of the mixture

solidified by standing for several months. All our attempts to free the oily product completely from the tribromnitroresorcine diethyl-ether have failed, so that we are unable to give any account of its composition.

Products soluble in Water.—In purifying the products of the action of sodic ethylate upon tribromtrinitrobenzol, the aqueous solution formed by washing the residue from spontaneous evaporation contained a large amount of organic matter, as was indicated by its orange-red color. In order to determine its nature, the solution was acidified with dilute sulphuric acid, which gave a precipitate, but did not remove all the organic matter present, since the filtrate still showed a strong yellow color. This precipitate was washed with water, in which it is nearly insoluble, until the washings ceased to show a yellow color, and then purified by converting it into its sodium salt, filtering the solution, reprecipitating with dilute sulphuric acid, and finally crystallizing from dilute alcohol until it showed the constant melting point 89° , when it was dried *in vacuo* and analyzed with the following results:—

0.2285 gr. of the substance gave on combustion 0.3145 gr. of carbonic dioxide and 0.0817 gr. of water.

	Calculated for $C_9(OC_2H_5)_2OH(NO_2)_3$.	Found.
Carbon	37.85	37.53
Hydrogen	3.47	3.97

To confirm these results, a portion of the substance was treated with an aqueous solution of less than the calculated amount of sodic hydrate necessary to convert it into the sodium salt, the solution of the salt was filtered from the unaltered phenol, the filtrate evaporated to dryness, and the residue washed with benzol to remove any traces of the free phenol which might have dissolved in the water. It was then dried at 100° , and the sodium salt thus obtained analyzed with the following results:—

I. 0.1498 gr. of the substance yielded 0.0329 gr. of sodic sulphate.

II. 0.2410 gr. of the salt gave 0.0524 gr. of sodic sulphate.

	Calculated for $C_9(OC_2H_5)_2ONa(NO_2)_3$.	Found.	
		I.	II.
Sodium	6.78	7.11	7.04

These analyses leave no doubt that the substance is the diethyl-ether of trinitrophenylglucine. As it has not been described heretofore, we add its properties.

Properties of the Diethylether of Trinitrophloroglucine. — This substance crystallizes in square-ended rather short prisms, or in longer flat needles, also usually with square ends, although sometimes instead of this they are very sharp; both forms are frequently arranged in fan-like groups. It has a straw-yellow color, and melts at 89°. Very freely soluble in ethyl or methyl alcohol, ether, benzol, glacial acetic acid, chloroform, or acetone; soluble in carbonic disulphide; very slightly soluble in ligroine; slightly soluble in cold water, more soluble in hot; dilute alcohol is the best solvent for it. The three strong acids have no apparent action on it, hot or cold. Sodid hydrate dissolves it, forming an orange-red sodium salt, which crystallizes in fine needles. Ammonic hydrate dissolves it rather slowly, forming a yellow solution. Solutions of sodic or acid sodic carbonate also dissolve it with evolution of carbonic dioxide forming yellow solutions; it is evident, therefore, that the substance possesses strongly acid properties.

The filtrate from the diethylether of trinitrophloroglucine, which had changed from red to yellow on acidification, after concentration on the water bath deposited upon cooling rather ragged thick yellow needles; but if the evaporation was carried on spontaneously, yellow hexagonal prisms were obtained, which dissolved in alkalis more easily than in water, and gave, according to the amount of alkali used, red or yellow salts, crystallizing in hair-like needles, properties which indicated that the substance was a polyatomic nitrophenol, probably the trinitrophloroglucine. This substance has been described by Benedikt * as crystallizing from water in hexagonal prisms, and melting at 158°; we accordingly purified our substance by crystallization from water, but found that it melted as high as 167°. In spite of the want of agreement between this melting point and that given by Benedikt, the crystalline form and other properties indicated that the substance was trinitrophloroglucine, and this was proved to be the case by the following analyses. As Benedikt found that trinitrophloroglucine contains one molecule of water of crystallization, we examined our substance for this.

I. 0.7721 gr. of the air-dried substance when heated to a temperature of 105° lost 0.0477 gr.

	Calculated for $C_6(OH)_3(NO_2)_3 \cdot H_2O$.	Found.
Water	6.45	I. 6.18

* Ber d. ch. Ges., XI. 1876.

The air-dried substance lost 0.0015 gr. at 56°, and showed a tendency to sublime at 105°.

- II. 0.2126 gr. of the compound dried at 105° gave on combustion 0.2105 gr. of carbonic dioxide and 0.0304 gr. of water.
 III. 0.2260 gr. of the compound dried at 105° gave 31.2 c.c. of nitrogen at a temperature of 17° and a pressure of 775.8 mm.

	Calculated for $C_6(OH)_3(NO_2)_3$	Found.	
		II.	III.
Carbon	27.58	27.01*	
Hydrogen	1.15	1.59	
Nitrogen	16.69		16.37

It is evident from these analyses that the substance is *trinitrophloroglucine*, and therefore it becomes important to explain the very marked difference between the melting points observed by Benedikt and by us. We are inclined to ascribe this to the water of crystallization, as the melting point 167° was obtained with the substance dried at 105° used for analysis, whereas with samples which had been only air dried (or dried at 50°) we obtained melting points as low as 160–161°, that is, only 2° or 3° above the 158° obtained by Benedikt.

In order to determine whether the formation of the trinitrophloroglucine and its diethylether was due to a direct reaction, or to the secondary reaction on the trinitrophloroglucine triethylether of some sodic hydrate formed by the moisture of the air acting on the sodic ethylate, the following experiment was tried. Absolute alcohol made in the usual way with quick-lime was treated with a small quantity of sodium, and then the unaltered alcohol distilled off from the sodic alcoholate in a perfectly dry apparatus, which communicated with the outer air only through a drying tube; to the distillate in the flask which served as a receiver, a quantity of bright sodium was added as quickly as possible, after which it was closed at once with a cork carrying a drying tube. When the reaction was at an end, and the solution of sodic ethylate had cooled, 5 gr. of dry tribromtrinitrobenzol were added, and the mixture allowed to stand over night closed with the cork carrying the drying tube. The solution, which had turned red, was acidified with dilute sulphuric

* The percentages of carbon and hydrogen are as near to those required by the formula as could be expected when the difficulty of making a combustion of this explosive substance is considered.

acid and allowed to evaporate spontaneously, when after purification it yielded 2 gr. of the triethylether of trinitrophloroglucine instead of 0.12 gr., the usual yield when no special precautions were taken to exclude atmospheric moisture. It is evident, therefore, that the trinitrophloroglucine triethylether is formed at first, and afterward saponified wholly or in part by sodic hydrate produced by the action of moisture on the sodic ethylate. That most of this sodic hydrate is formed during the spontaneous evaporation of the alkaline solution was shown by two experiments, in which the triethylether of trinitrophloroglucine was treated with a solution of sodic ethylate, with all the precautions described above, except that in one of these experiments the alkaline liquid was allowed to evaporate spontaneously, when all the triethylether was saponified, the whole product being soluble in water, whereas in the other, which was acidified before evaporating, 0.65 gr. of unaltered triethylether was recovered, 0.7 gr. having been the amount used.

Lobry de Bruyn* has encountered similar difficulties in studying the action of sodic ethylate upon the unsymmetrical trinitrobenzol (1, 2, 4), as in this case considerable quantities of dinitrophenol were obtained, whereas with sodic methylate the dinitroanisol was the only organic product.

Experiments with Acetic Ester as the Solvent.

After we had found that the presence of benzol diminished the tendency of sodic ethylate to replace nitro groups in the tribromtrinitrobenzol, we tried some experiments on the action of other solvents. The choice here however was limited, because there are so few liquids belonging to a different class from benzol which have any considerable solvent action on the tribromtrinitrobenzol; in fact, acetone and acetic ester were the only ones easily obtained which fulfilled this condition, and acetone had to be rejected, as it seemed to take part in the reaction, giving a dark brownish red solution, very different from the orange-red obtained in all other cases. This result was not unexpected after the work of Freer,† published only in the preliminary paper at the time we tried this experiment, and since we did this work we have seen the paper of Janovsky,‡ describing the colors which he obtained by the action of

* Rec. Trav. Chim. des Pays-Bas, IX. 191.

† Am. Chem. Journ., XII. 355; XIII. 308, Freer and Higley; XIII. 322.

‡ Ber. d. ch. Ges., 1891, p. 971.

acetone and potassic hydrate on dinitro compounds of the aromatic series.

In our first experiment with acetic ester we used the commercial article without specially drying it. The action was carried on in the usual way, 5 gr. of tribromtrinitrobenzol being used. The aqueous washings gave tests for nitrite and bromide, but the organic product was found to consist principally of the tribromdinitrophenetol melting at 147° , described in our previous paper.* For greater certainty it was analyzed, with the following results:—

- I. 0.2972 gr. of the substance gave by the method of Carius
0.3721 gr. of argentic bromide.
II. 0.2788 gr. of the substance gave 0.3535 gr. of argentic
bromide.

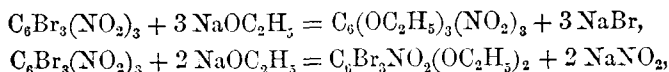
	Calculated for $C_6Br_3(NO_2)_2OC_2H_5$.	Found.	
		I.	II.
Bromine	53.46	53.27	53.96

This experiment called our attention to a subject which we had already studied without any very definite result, that is, the conditions under which the phenetol $C_6Br_3(NO_2)_2OC_2H_5$ is formed, rather than the tribromnitroresorcine diethylether, $C_6Br_3NO_2(OC_2H_5)_2$. Our previous work had led us to the conclusion that the presence of a trace of water is favorable to the formation of the phenetol, as on one occasion when benzol not dried over sodium was used this substance was obtained, and in the experiment described in our previous paper which yielded a quantity of the phenetol common benzol was also used, whereas in all the preparations made by us with absolute benzol and alcohol not a trace of the phenetol has been found. On the other hand, in a repetition of the experiment with common benzol, and in one in which undried benzol and common instead of absolute alcohol were used only the resorcine ether $C_6Br_3NO_2(OC_2H_5)_2$ was isolated. To test this question still further, we repeated the experiment described at the beginning of this section, using carefully dried acetic ester instead of the commercial article, and obtained decidedly less of the phenetol with a large proportion of the tribromnitroresorcine diethylether, thus confirming, although not absolutely proving, our previous inference that the presence of a trace of moisture is favorable to the formation of the phenetol.

* These Proceedings, XXV. 185.

Action when Alcohol is the only Solvent used.

This action has been already described in our first paper, but after we had found, as described in the preceding sections, that the action when benzol was present took place in the two parallel reactions,



it became of interest to determine whether the first of these reactions took place if alcohol was the only solvent, or whether the action consisted of the second alone, as we had supposed when we published our first paper. A very little work was sufficient to prove the presence of the trinitrophenylglucine triethylether, or the phenols formed by its saponification, among the products of the reaction when alcohol was the only solvent, thus showing that the action in the two cases is parallel, although the first reaction takes place to a much more limited extent when alcohol is the only solvent, than when a mixture of alcohol and benzol is used. Our attempts to determine the relative amounts of the products of each of these two reactions are described in a later section.

Preparation of Tribromnitroresorcine Diethylether and Trinitrophenylglucine Triethylether.

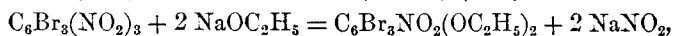
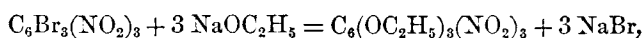
It follows from what has been said in the preceding sections, that the best way to prepare tribromnitroresorcine diethylether is to allow tribromtrinitrobenzol (10 parts) to stand in the cold for twelve hours with an alcoholic solution of sodic ethylate (from 1.5 parts of sodium), then, after the solvent has evaporated spontaneously, to wash the residue with water, and after one crystallization of the insoluble part from alcohol treat it in the cold with an alcoholic solution of sodic hydrate for about twelve hours to saponify the trinitrophenylglucine triethylether also present. The sodium salt thus formed is washed out, and the residue crystallized from alcohol until it shows the melting point of 101° .

If, on the other hand, trinitrophenylglucine triethylether is to be prepared, the tribromtrinitrobenzol should be dissolved in anhydrous benzol (dried with sodium) and the alcoholic solution of sodic ethylate added to this solution. Every precaution should be taken to exclude even traces of moisture, and after the twelve hours standing the solution should be acidified with dilute sulphuric acid

before allowing it to evaporate spontaneously. The residue, after washing with water, is purified by crystallization from alcohol, which separates the two ethers formed by the parallel reactions.

*Quantitative Study of the Action of Sodie Ethylate on
Tribromtrinitrobenzol.*

After we had proved that this action takes place in these two different ways,



it became of interest to determine the relative extent of each of the parallel reactions under varying conditions, and the easiest way to do this was obviously to find the amount of sodic bromide and sodic nitrite formed, as the first must have proceeded from the reaction giving the trinitrophenyl glucine triethylether, the second from that producing the tribromnitroresorcine diethylether. In addition to this we have weighed the amount of organic matter formed, and have made some not very successful attempts to determine the amount of its several constituents. The method adopted was the following. A weighed quantity of tribromtrinitrobenzol mixed with the solvent and the ethylate in the proportion of three atoms of sodium to each molecule stood over night in a corked flask. The liquid was then allowed to evaporate spontaneously, and the residue washed thoroughly with water. The weight of the organic matter insoluble in water was taken, and also that of the aqueous solution which contained all the sodium salts; this was then divided into weighed parts, one of which was acidified with nitric acid, and after filtering out and weighing the diethylether of trinitrophenyl glucine the amount of sodic bromide it contained was determined with argentic nitrate. The second portion of the aqueous liquid was used for the determination of the amount of sodic nitrite, but it was not easy to find a method which would be applicable in this case. The common way of determining a nitrite with potassic permanganate was inadmissible, because of the presence of organic matter. The urea method in its usual form was also inapplicable because of the presence of sodic carbonate, but finally by modifying it in the following way we succeeded in obtaining satisfactory results. The weighed portion of the solution to be tested, mixed with a sufficient quantity of urea, was poured into a little flask, and a small test-tube containing dilute sulphuric acid put into the flask supported in a vertical

position by a piece of platinum wire projecting from its upper end and resting against the neck of the flask. The apparatus was then filled with carbonic dioxide from a heated tube containing magnesite, after which by shaking the flask the sulphuric acid was added to its contents in small quantities at a time, and the nitrogen given off collected over a solution of potassic hydrate, and measured in the usual way. It is necessary to heat the flask gently toward the end of the operation to drive off all the nitrogen. One half of the nitrogen collected is derived from the sodic nitrite. To test the accuracy of the method two determinations of the nitrogen in commercial sodic nitrite were made by it which gave, —

Nitrogen	Found.	
	18.09	18.11

and as they agreed with each other, and came tolerably near to the usual percentage of nitrogen in commercial sodic nitrite (between 19 and 20 per cent), it was evident that the method was accurate enough for our purposes. A third portion of the aqueous liquid was in two experiments used for the determination of the trinitrophloroglucine, but we give our results with a great deal of hesitation, as we were unable to find any satisfactory quantitative method; methods based upon extraction with an organic solvent, or the precipitation of the barium salt, which Benedikt says is insoluble, led to no result. We were therefore driven to determining the amount of nitrogen in the residue obtained by evaporating to dryness a portion of the aqueous solution acidified with sulphuric acid, and calculating from this the amount of trinitrophloroglucine, on the assumption, which at best can be but approximately correct, that this was the only substance containing nitrogen left in the residue.

Experiments in which Alcohol was the only Solvent used. —

I. Weight taken, 10.556 gr. Weight of aqueous solution, 135.4 gr.; 8.6 gr. of the solution gave 16.9 c.c. of nitrogen from the sodic nitrite under a temperature of 23° and a pressure of 763.8 mm.; 23.2 gr. of the solution gave 1.1718 gr. of argentic bromide; 20.8 gr. of the solution gave after the nitrous acid had been expelled by sulphuric acid 8.2 c.c. of nitrogen at a temperature of 23° and a pressure of 767.8 mm.; 54.4 gr. of the solution gave 0.808 gr. of the diethylether of trinitrophloroglucine. The organic matter insoluble in water weighed 6.97 gr.

II. Weight taken, 10.1582 gr. Weight of aqueous solution, 164.55 gr.; 15.95 gr. of the solution gave 24.65 c.c. of nitrogen

from the sodic nitrite at a temperature of $26^{\circ}.5$, and a pressure of 765 mm.; 58.45 gr. of the solution gave 1.6583 gr. of argentic bromide, and yielded 0.8499 gr. of the diethylether of trinitrophloroglucine. The organic matter insoluble in water weighed 5.78 gr.

III. Weight taken, 1.0366 gr. Weight of aqueous solution, 121.4 gr.; 62.5 gr. of the solution gave 13.6 c. c. of nitrogen from the sodic nitrite at a temperature of 21° and a pressure of 765.2 mm.; 58.9 gr. of the solution gave 0.2700 gr. of argentic bromide. The organic matter insoluble in water weighed 0.48 gr.

IV. Weight taken, 10 gr.* Weight of aqueous solution 142.9 gr.; 13.7 gr. of the solution gave 25.7 c.c. of nitrogen from the sodic nitrite at a temperature of $29^{\circ}.5$ and a pressure of 759.2 mm.; 55.1 gr. of the solution gave 1.9029 gr. of argentic bromide; 1.7 gr. of the diethylether of trinitrophloroglucine were obtained from the 10 gr. used. The weight of organic matter insoluble in water was 6.4 gr.

V. Weight taken, 10 gr.* Weight of aqueous solution, 114.8 gr.; 14.6 gr. of the solution gave 32.3 c.c. of nitrogen from the sodic nitrite at a temperature of 28° and a pressure of 764.1 mm.; 48.7 gr. of the solution gave 0.9573 gr. of argentic bromide; 2.4 gr. of the diethylether of trinitrophloroglucine were obtained from the 10 gr. used. The weight of organic matter insoluble in water was 5.6 gr.

The results of these experiments are given in tabular form at the end of the next section.

Experiments in which Benzol was the Principal Solvent used.—

VI. Weight taken, 10.0220 gr. Weight of aqueous solution, 126.65 gr.; 11.7 gr. of the solution gave 17.15 c. c. of nitrogen from the sodic nitrite at a temperature of 24° and a pressure of 764.5 mm.; 28.7 gr. of the solution gave 1.6952 gr. of argentic bromide; 24.7 gr. of the solution gave after the nitrous acid had been expelled by sulphuric acid 12.2 c. c. of nitrogen at a temperature of 25° and a pressure of 766.1 mm. The acid precipitated from these 24.7 gr. of the solution 0.3374 gr. of the diethylether of trinitrophloroglucine. The organic matter insoluble in water weighed 4.99 gr.

VII. Weight taken, 10.1976 gr. Weight of aqueous solution, 135.2 gr.; 19.3 gr. of the solution gave 27.2 c. c. of nitrogen from the sodic nitrite at a temperature of 25° and a pressure of 750.9 mm.; 43.9 gr. of the solution gave 1.6158 gr. of argentic

* This weight is accurate only to tenths of a gram.

bromide; 72 gr. of the solution gave 1.4724 gr. of the diethylether of trinitrophloroglucine. The organic matter insoluble in water weighed 5.51 gr.

VIII. Weight taken, 1.2524 gr. Weight of aqueous solution, 37.3 gr.; 24.2 gr. of the solution gave 14.3 c.c. of nitrogen from the sodic nitrite at a temperature of 19° and a pressure of 771.5 mm.; 13.1 gr. of the solution gave 0.4097 gr. of argentic bromide. The organic matter insoluble in water weighed 0.55 gr.

IX. Weight taken, 1.2682 gr. Weight of the aqueous solution, 38.1 gr.; 19.7 gr. of the solution gave 12 c.c. of nitrogen from the sodic nitrite at a temperature of 24° and a pressure of 767.3 mm.; 18.4 gr. of the solution gave 0.5082 gr. of argentic bromide. The organic matter insoluble in water weighed 0.53 gr.

X. Weight taken, 1.2287 gr. Weight of the aqueous solution, 53.65 gr.; 17.65 gr. of the solution gave 7.7 c. c. of nitrogen from the sodic nitrite at a temperature of 25° and a pressure of 766.1 mm.; 18.9 gr. of the solution gave 0.2664 gr. of argentic bromide, and 0.0854 gr. of the diethylether of trinitrophloroglucine. The organic matter insoluble in water weighed 0.63 gr.

In the following tables the first column gives the number of the experiment, and the weight of tribromtrinitrobenzol used; the second, the percentage of nitrogen removed as sodic nitrite referred to the total amount of nitrogen which could be removed from the tribromtrinitrobenzol by this reaction, that is, two out of the three atoms of nitrogen, because the product $C_6Br_3NO_2(OC_2H_5)_2$ contains one nitro group; the third column gives the percentage of the total bromine removed as sodic bromide; the fourth, the weight of the organic matter insoluble in water; the fifth, the weight of the diethylether of trinitrophloroglucine; and the sixth, the weight of trinitrophloroglucine calculated from the volume of nitrogen obtained from the residue after acidification with sulphuric acid.

TABLE I.—ACTION OF SODIC ETHYLATE IN ETHYL ALCOHOL.

	Weight of $C_6Br_3(NO_2)_3$ used.	Per Cent of Nitrogen.	Per Cent of Bromine.	Weight of Organic Matter.	Weight of $C_6(OC_2H_5)_2OH$ (NO_2) ₂	Weight of $C_6(OH)_3NO_2$
I.	10.556	45.88	42.53	6.97	2.0	0.38
II.	10.1582	44.85	36.67	5.78	2.39	
III.	1.0366	46.95	42.85	0.48		
IV.	10.	46.86	39.39	6.4	1.7	
V.	10.	45.06	18.02	5.6	2.4	

TABLE II. — ACTION OF SODIC ETHYLATE WITH BENZOL AND ALCOHOL.

	Weight of $C_6Br_3(NO_2)_3$	Per Cent of Nitrogen.	Per Cent of Bromine.	Weight of Organic Matter.	Weight of $C_6(OC_2H_5)_2OH$ (NO_2) ₃	Weight of $C_6(OH)_3(NO_2)_3$
VI.	10.022	33.58	59.54	4.99	1.73	0.44
VII.	10.1976	33.09	38.91	5.51	2.8	
VIII.	1.2524	33.03	74.32	0.55		
IX.	1.2682	33.31	66.21	0.58		
X.	1.2287	34.42	49.10	0.68		

An examination of these tables shows that the percentages of nitrogen removed are fairly constant under each set of conditions, the maximum differences being, in Table I., 2.1 per cent, in Table II., 1.39 per cent,— which are surprisingly small when the nature of the process and the roughness of the manipulations are considered. These numbers, therefore, are well fitted to give an idea of the effect on the reactions of the presence of benzol, and they show that it diminishes the amount of sodic nitrite formed, since the percentage of nitrogen removed when alcohol alone is present averages 45.92 (maximum 46.95, minimum 44.85), whereas if the solvent is partly benzol the average percentage falls to 33.49 (maximum 34.42, minimum 33.03).

On the other hand, no agreement is found in the amounts of bromine removed as sodic bromide, the maximum difference in Table I. being 24.83 per cent, in Table II. 35.41 per cent; but in spite of this these results show that the presence of benzol favors the removal of bromine, since of the five determinations of bromine in presence of benzol (Table II.), only one (38.91 per cent) is below the largest percentage of bromine obtained (42.85 per cent) when alcohol was the only solvent (Table I.), and most of those in Table II. are very far above those in Table I.

As to the numerical relations between the percentages of inorganic compounds formed under the two sets of conditions, it is to be observed that in the alcohol series the amounts of nitrite and bromide are approximately equal. In the benzol series the amount of nitrite is almost exactly one third of the total amount which could have been formed, and is in some cases about one half that of the

bromide. In most cases, between 80 and 90 per cent of the tribrom-trinitrobenzol used is accounted for by the amounts of inorganic salts formed. The experimental work is not accurate enough to allow a more careful discussion of this part of the subject, as not enough attention was paid to various details, such, for instance, as maintaining a constant temperature, and measuring accurately the amounts of solvent used.

In all the experiments with benzol given in Table II. free alcohol was also present. To determine what influence this had on the reaction, we made another experiment, in which all free alcohol was carefully excluded, so that in this case benzol was the only liquid present.

XI. Weight taken, 5.0453 gr. Weight of the aqueous solution, 83.4 gr.; 19.6 gr. of the solution gave 23.8 c. c. of nitrogen at a temperature of $28^{\circ}.5$ and a pressure of 760.1 mm.; 43.4 gr. of the solution gave 1.9610 gr. of argentic bromide and 1.55 gr. of the diethylether of trinitrophloroglucine. The organic matter insoluble in water weighed 2.75 gr.

From these results 35.34 per cent of nitrogen and 59.62 per cent of bromine are obtained. The percentage of nitrogen, when benzol and alcohol were used as the solvents, averaged 33.49, so that this experiment shows that the presence of alcohol does not materially affect the result. The somewhat high percentage of nitrogen in this experiment may be due to the fact that the mixture stood two days instead of the usual twelve hours. This subject of the effect of time on the action will be discussed later in the paper.

We have also made two quantitative determinations, in which acetic ester was used with a little alcohol as the solvent.

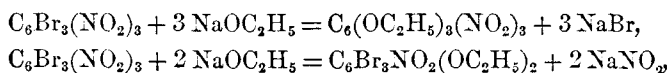
XII. Weight taken, 1.0412 gr. Weight of the aqueous solution, 58 gr.; 17.5 gr. of the solution gave 0.63 c. c. of nitrogen at a temperature of $23^{\circ}.5$ and a pressure of 758.9 mm.; 40.5 gr. of the solution gave 0.4504 gr. of argentic bromide.

XIII. Weight taken, 1.0271 gr. Weight of the aqueous solution, 49.1 gr.; 18 gr. of the solution gave 2.8 c. c. of nitrogen at a temperature of $22^{\circ}.5$ and a pressure of 760.8 mm.; 31.1 gr. of the solution gave 0.4902 gr. of argentic bromide.

	Per Cent of Nitrogen.	Per Cent of Bromine.
XII. 1.0412	3.62	50.06
XIII. 1.0271	13.49	60.15

We are inclined to regard No. XII. with suspicion; but No. XIII. alone shows that acetic ester has an even more unfavorable influence than benzol on the formation of the sodic nitrite; this is probably due to the fact that in this case there is a tendency to form the tribromdinitrophenetol, which would yield half as much sodic nitrite as the tribrommonitroresorcine diethylether formed when benzol was used.

Relative Yields of the Organic Products. — After we had determined the amounts of sodic bromide and nitrite formed by the two parallel reactions,



we tried to get an idea of the relative yields of the organic products. This could be done with some approach to accuracy in the case of the reaction which produces sodic bromide, because during the work most of the trinitrophloroglucine triethylether was converted into the salts of trinitrophloroglucine or its diethylether, both of which can be easily separated from the other organic products on account of their solubility in water. With the tribromnitroresorcine diethylether on the other hand, no such approach to accuracy was obtained, because it could be purified only by crystallization, and a large portion of it remained mixed with the viscous impurity already mentioned. To obtain the following results, the organic matter insoluble in water obtained from two experiments was repeatedly crystallized from alcohol, until as much pure tribromnitroresorcine diethylether and trinitrophloroglucine triethylether had been obtained as possible. To the amount of the latter, which was very small, were added the calculated amounts of the triethylether corresponding to the quantities found of free trinitrophloroglucine and its diethylether. Two pairs of experiments were studied in this way, one from the series in which alcohol was the only solvent, and one from that in which benzol was used.

Experiments I. and II. — Alcohol the only solvent. 20.71 gr. of tribromtrinitrobenzol gave 12.75 gr. of organic matter insoluble in water, from which were obtained 5.11 gr. of $\text{C}_6\text{Br}_3\text{NO}_2(\text{OC}_2\text{H}_5)_2$, 1.4 gr. of the same slightly impure, 5.1 gr. of the semi-liquid fraction from the mother liquor, and 0.49 gr. of $\text{C}_6(\text{OC}_2\text{H}_5)_3(\text{NO}_2)_3$. From the aqueous solution 4.39 gr. of $\text{C}_6\text{OH}(\text{OC}_2\text{H}_5)_2(\text{NO}_2)_3$ were obtained, corresponding to 4.77 gr. of the triethylether, and

0.78 gr.* of $C_6(OH)_3(NO_2)_3$, corresponding to 1.03 gr. of the triethylether, making the total yield of the triethylether 6.29 gr.

Experiments VI. and VII. — Benzol present, 20.21 gr. of tribromtrinitrobenzol gave 10.50 gr. of organic matter insoluble in water from which were obtained 3.25 gr. of $C_6Br_3NO_2(OC_2H_5)_2$, 1.36 gr. of $C_6(OC_2H_5)_3(NO_2)_3$, and somewhat less than 6 gr. of the semi-liquid fraction from the mother liquors. From the aqueous solution were obtained 4.53 gr. of $C_6OH(OC_2H_5)_2(NO_2)_3$, corresponding to 4.93 gr. of the triethylether, and 0.88 gr.* of $C_6(OH)_3(NO_2)_3$, corresponding to 1.16 gr. of the triethylether, making the total yield of the triethylether 7.45 gr.

These results confirm the inference drawn from the percentage, of sodic nitrite and bromide, that the presence of benzol is unfavorable to the reaction by which sodic nitrite is formed, but promotes that which yields sodic bromide; a fact which is shown more plainly by this collection of the results in tabular form.

	$C_6(OC_2H_5)_3(NO_2)_3$.	$C_6Br_3NO_2(OC_2H_5)_2$
Alcohol alone (I. and II.)	6.29 gr.	5.11†
Benzol and alcohol (VI. and VII.)	7.45 gr.	3.25†

All our results, therefore, show that the presence of benzol is favorable to the elimination of bromine, unfavorable to that of nitro groups. The most probable theoretical explanation of this observation which has occurred to us depends on the effect of the change of solvents upon the amounts of the salts precipitated, but any discussion of this theory at present would not be worth while, because the principle on which it rests has not been tested by experiment so far as we can find.

We have not succeeded in finding the cause of the very marked variations in the amounts of sodic bromide shown in Tables I. and II. At first we feared they might be due to defects in our experimental work, but that this is not the case is shown by the following comparison of the weights of trinitrophloroglucine triethylether actually found with the amounts of this substance calculated from the percentages of bromine eliminated as sodic bromide in the same experiment. We have selected this body for the comparison, be-

* These numbers are only estimates, as the amounts of trinitrophloroglucine were determined only in Nos. I. and VI., the weight found being doubled to give the numbers. It is to be remembered also that our method for determining the trinitrophloroglucine was far from satisfactory.

† These numbers are only approximations to the true yields.

cause, as has been already stated, these weights were determined with a fair degree of accuracy.

	Calculated	Found.
Alcohol alone (I. and II.)	6.30	6.29
Alcohol and benzol (VI. and VII.)	7.62	7.45

The agreement is much closer than we had any right to expect, and shows that the differences in the percentages of bromine are due to absolute variations in the extent of the reaction by which the bromine is removed, since experiments VI. and VII. differ in this respect very widely (VI. 59.54 per cent of bromine, VII. 38.91 per cent of bromine); and yet the amount of the trinitrophloroglucine triethylether calculated from these different percentages of bromine corresponds almost exactly to that obtained experimentally.

PART II.

ACTION OF OTHER ALCOHOLATES ON TRIBROMTRINITROBENZOL.

In addition to the work with sodic ethylate just described, we have tried the action of the sodium compounds of other alcohols on the tribromtrinitrobenzol, and give in the first place descriptions of the new compounds thus obtained, followed by a series of quantitative experiments similar to those tried with the ethylate.

Sodic Methylate.

The organic compound insoluble in water obtained by the action of sodic methylate on tribromtrinitrobenzol consisted in every experiment we have tried of the tribromnitroresorcine dimethylether, melting at 126°, and already described in our first paper;* as, however, we found that a considerable amount of sodic bromide was formed in these experiments, we turned our attention to the aqueous washings of this organic matter, in which it was evident that the product formed by the removal of the bromine was to be sought. Upon acidifying this aqueous solution with dilute sulphuric acid, a copious precipitate was obtained, which was only slightly soluble in water, and was purified by crystallization with the following precautions. The substance was dissolved in as small

* These Proceedings, XXV. 186.

a quantity as possible of cold alcohol, water was then added until it began to grow turbid, when the solution was cleared by the addition of a drop or two of alcohol, and allowed to evaporate spontaneously, all these operations being carried on in the cold. When it showed the constant melting point $77-78^{\circ}$, it was dried and analyzed with the following results:—

0.2298 gr. of the substance gave on combustion 0.2792 gr. of carbonic dioxide and 0.0597 gr. of water.

	Calculated for $C_6(OCH_3)_2OH(NO_2)_3$.	Found.
Carbon	33.22	33.13
Hydrogen	2.42	2.89

To confirm this result the sodium salt was made and analyzed; for this purpose 1 gr. of the substance was treated with 0.1 gr. of sodic hydrate dissolved in a little water, that is, decidedly less sodic hydrate than would be needed to convert the whole of the substance into its salt. The yellow solution thus obtained was evaporated to dryness at 100° , washed with benzol to remove the small quantity of the free phenol which had dissolved in the water, dried at 100° , and analyzed with the following result:—

0.3730 gr. of the salt gave 0.0874 gr. of sodic sulphate.

	Calculated for $C_6(OCH_3)_2ONa(NO_2)_3$.	Found
Sodium	7.39	7.59

These analyses and the analogy with the corresponding ethyl compound leave no doubt that the substance is the dimethylether of trinitrophloroglucine.

Properties of the Dimethylether of Trinitrophloroglucine, $C_6(OCH_3)_2OH(NO_2)_3$.—The substance crystallizes with the precautions given above in long slender needles, with a slightly yellowish tinge, which melt at $77-78^{\circ}$, and are very soluble in ethyl alcohol, methyl alcohol, ether, benzol, chloroform, acetone, or glacial acetic acid; soluble in carbonic disulphide; slightly soluble in ligroine; somewhat soluble in cold water, more soluble in hot. With alkalis it forms reddish yellow salts. Strong sulphuric or hydrochloric acid does not act on it; it dissolves in strong nitric acid, but seems to be precipitated unchanged by dilution.

We also obtained a small amount of another substance with a higher melting point, but not in sufficient quantity to characterize it.

Action of Sodid Propylate on Tribromtrinitrobenzol.

4 gr. of normal propyl alcohol were mixed with anhydrous benzol, and treated with 1.5 gr. of metallic sodium until all the sodium had disappeared; the reaction ran slowly, and was assisted by a gentle heat. The sodic propylate thus obtained was carefully cooled, and then a benzol solution of 10 gr. of tribromtrinitrobenzol added in small portions at a time, shaking and cooling with water after each addition. The proportions are about three atoms of sodium and three molecules of propyl alcohol to each molecule of tribromtrinitrobenzol. As the first portions of the solutions were mixed the liquid turned blood-red, and this color, which at first faded to yellow on shaking, became permanent as more of the solution of tribromtrinitrobenzol was added. The mixture, which at no time showed a rise of temperature, was allowed to stand over night in a corked flask, and then the solution was filtered from a deposit of solid matter, which, after drying off the benzol, gave tests for a bromide and a nitrite. The benzol solution to which the solid not used for the above tests had been added was treated with water, and then acidified with dilute sulphuric acid, washed thoroughly, and, after most of the benzol had been recovered by distillation, the rest was distilled off in a current of steam. The residue thus obtained was oily, but solidified after standing for some time; it was then purified by crystallization from alcohol until it showed the constant melting point 109–110°, when it was dried at about 70°, and analyzed with the following results:—

0.2366 gr. of the substance gave on combustion 0.4058 gr. of carbonic dioxide and 0.1214 gr. of water.

	Calculated for $C_6(OC_3H_7)_3(NO_2)_3$.	Found.
Carbon	46.51	46.78
Hydrogen	5.43	5.70

The substance gives no test for bromine when heated on a copper wire. These results prove that it is the normal propylether of trinitrophenol.

The aqueous solution, acidified with sulphuric acid, from which the benzol had been separated gave on extraction with ether a small amount of a yellow substance, which seemed to be trinitrophenol, but was not present in sufficient amount for complete identification.

Properties of the Normal Tripropylether of Trinitrophloroglucine, $C_6(OC_3H_7)_3(NO_2)_3$. — This substance crystallizes in plates often as much as three millimeters long and one broad, which under the microscope are seen to be made up of a number of flat prisms with square ends united by their longer sides, and usually much striated on lines parallel to both sets of edges. Its color is white with a very slight yellowish tinge, and it turns yellowish brown on standing exposed to the air. It melts at $109-110^\circ$, and is soluble in cold ethyl or methyl alcohol, more freely when hot; freely soluble in ether, benzol, chloroform, acetone, or carbonic disulphide; soluble in glacial acetic acid; slightly soluble in ligroine, or in water whether hot or cold. Neither strong sulphuric, strong nitric, nor strong hydrochloric acid has any apparent action on it, whether cold or hot. The best solvent for it is boiling alcohol.

In another experiment no benzol was used, but the tribromtrinitrobenzol suspended in propyl alcohol was treated with sodic propylate. The product in this case was an oil which did not solidify even after standing for three months. We accordingly tried to purify it by treatment with a cold solution of sodic hydrate, and in this way obtained an orange solution, from which trinitrophloroglucine was easily isolated, pointing to the presence of the tripropyl ether of this body in the oil. After we could obtain no more of the sodium salt of the trinitrophloroglucine by further action of sodic hydrate, the oil was washed with water, dissolved in alcohol, precipitated again with water, and dried at 100° , when we hoped an analysis might throw some light on its composition; but in this we were disappointed, as a determination of the amount of bromine gave 45.29 per cent, whereas the tribromnitroresorcine dipropylether, which we hoped might have been formed, should contain 50.42 per cent. of bromine. As we could find no better way of purifying this substance, we have been forced to leave undecided the nature of the product formed by the replacement of nitro groups in tribromtrinitrobenzol by propoxy radicals. Fortunately, it is not a point of great importance.

Action of Sodic Isopropylate on Tribromtrinitrobenzol.

4 gr. of isopropyl alcohol were converted into its sodium compound by treatment with 1.5 gr. of sodium in anhydrous benzol, when it was found that the isopropyl alcohol acts on sodium more energetically than normal propyl alcohol, but both act less readily than ethyl alcohol. The isopropylate thus obtained was allowed to

act on 10 gr. of tribromtrinitrobenzol under the conditions described in the preceding section. The phenomena observed in this case were the same as those described for the normal propylate except that a slight rise of temperature from the reaction was observed. The solid deposited over night gave a strong test for sodic bromide and a distinct test for sodic nitrite. The principal organic product was obtained and purified in the way given under the normal propyl compound until it showed the constant melting point 130° , when it was dried at 100° , and analyzed with the following results:—

0.2280 gr. of the substance gave on combustion 0.3876 gr. of carbonic dioxide and 0.1182 gr. of water.

	Calculated for $C_6(OC_3H_7)_3(NO_2)_3$.	Found.
Carbon	46.51	46.36
Hydrogen	5.43	5.76

The substance gave no test for bromine when heated with cupric oxide. A small amount of trinitrophenol seemed to be formed as a secondary product in preparing the substance analyzed above.

Properties of the Triisopropylether of Trinitrophenol. $C_6(OC_3H_7)_3(NO_2)_3$. — This substance crystallizes in plates often one centimeter long, made up of flattened prisms united by their longer sides. These prisms are terminated by two planes at an obtuse angle to each other, and seem to belong to the monoclinic system. It is white when first prepared, but gradually takes on an orange color on exposure to the air. It melts at 130° , and is not very soluble in cold ethyl or methyl alcohol, more soluble in hot; very soluble in benzol or chloroform; freely in ether, or acetone; soluble in carbonic disulphide; slightly soluble in cold glacial acetic acid, freely when hot; very slightly soluble in ligroine, and nearly insoluble in water whether cold or hot. The three strong acids have no apparent action on it whether cold or hot. The best solvent for it is boiling alcohol.

Action of Sodic Benzylate on Tribromtrinitrobenzol.

The sodic benzylate used was prepared as follows. To 1.3 gr. of sodium mixed with anhydrous benzol and heated in a flask with a return condenser, 6.5 gr. of benzyl alcohol were added in small quantities at a time, and the heating continued until all the sodium had disappeared, which usually was not till after four hours. The

benzyl alcohol therefore acts with sodium much more slowly than any of the other alcohols used by us. In this way we obtained a benzol * solution of the sodic benzyrate, which remained clear after it had cooled until it was shaken, when the solid separated in a gelatinous state. To the mixture of gelatinous sodic benzyrate and benzol thus obtained a benzol solution of 9 gr. of tribromtrinitrobenzol was added; that is, for each molecule of tribromtrinitrobenzol we used three molecules of sodic benzyrate.† The mixture was allowed to stand in the cold over night, the orange-red solution thus formed evaporated to dryness on a steam radiator at temperatures below 70°, and the residue washed with water and afterward with alcohol, after which it was purified by crystallization from a mixture of benzol and alcohol, until it showed the constant melting point 171°. The analyses of the substance dried at 100° gave the following results:—

- I. 0.2038 gr. of the substance gave on combustion 0.4546 gr. of carbonic dioxide and 0.0752 gr. of water.
- II. 0.2678 gr. of the substance gave 18.8 c.c. of nitrogen at a temperature of 25° and a pressure of 765.3 mm.

	Calculated for $C_6(OC_7H_7)_3(NO_2)_3$.	Found.	
		I.	II.
Carbon	61.01	60.84	
Hydrogen	3.96	4.10	
Nitrogen	7.91		7.89

The substance gave no test for bromine when heated with cupric oxide.

10 gr. of tribromtrinitrobenzol gave only 1.5 gr. of the tribenzylether of trinitrophenylglucine, the analysis of which is given above, that is, less than 13 per cent of the theoretical yield. This substance, therefore, is not by any means the principal product of the reaction. What the other products are will be discussed after the description of the properties of the benzyether.

Properties of the Trinitrophenylglucine Tribenzylether. — This substance crystallizes from a mixture of alcohol and benzol in slen-

* Since this part of our work was finished, Brühl and Biltz have published similar observations on other alcoholates in Ber. d. ch. Ges., XXI. 649 (1891).

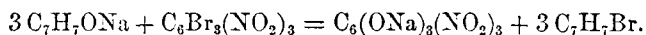
† The same principal product was obtained in a subsequent experiment with only two molecules of sodic benzyrate. In most cases a slight excess of benzyl alcohol was used.

der white needles forming a thick mat. It turns yellowish brown on exposure to the air, and melts at 171° ; is slightly soluble even in hot alcohol, less soluble still in cold; somewhat more soluble in methyl than in ethyl alcohol; very freely soluble in benzol, chloroform, or acetone; freely in carbonic disulphide; soluble in glacial acetic acid; very slightly soluble in ligroine; essentially insoluble in water, whether cold or hot. The best solvent for it is a mixture of alcohol and benzol. Strong sulphuric acid does not seem to act on it until charring sets in; strong nitric acid does not act on it in the cold, but seems to oxidize it when hot; strong hydrochloric acid has no apparent action on it, hot or cold.

Other Products of the Action of Sodid Benzylate on Tribromtrinitrobenzol.—To obtain these substances the aqueous and alcoholic washings mentioned above were evaporated to dryness, and the oily portion separated by extraction with a little alcohol from the salts. These, it was found, were a mixture of the sodium salt of trinitrophloroglucine with sodic bromide and nitrite, from which the trinitrophloroglucine was easily obtained, and identified by the melting point 167° , and by analysis. It is one of the principal products of the reaction, and in fact most of the trinitrophloroglucine used for the analyses given in the first part of this paper was obtained in this way.

The oily material separated by the alcohol consisted mostly of the excess of benzyl alcohol, but on warming it we perceived the smell of benzyl bromide, and also suffered from its violent action on the eyes. Accordingly some of it, carefully washed to remove any sodic bromide, was boiled with an alcoholic solution of sodic sulphide, when it gave a strong smell of benzyl sulphide, and the water with which it was washed gave a faint test for bromine with chlorine water. We did not succeed, however, in isolating the benzyl sulphide, which at best must have been present in very small quantity. Another similar oil, after thorough washing with water, was boiled with sodic acetate and alcohol, then water was added, which after being freed from the organic matter gave a slight test for bromine with chlorine water. In another experiment the original product, after acidification with dilute sulphuric acid, was distilled with steam, and the oily distillate, having been thoroughly washed with water, was boiled with alcoholic sodic acetate, when it yielded a very strong test for a bromide with chlorine water. These experiments have convinced us that in these three preparations a small quantity of benzyl bromide was present in the product of the reac-

tion, although we have not succeeded in isolating the benzyl bromide itself, or one of its derivatives. This did not proceed from an impurity of benzyl bromide in the benzyl alcohol used, since after boiling it with an alcoholic solution of sodic acetate no test for sodic bromide could be obtained; it must have been formed, therefore, either in the course of the reaction, or in the subsequent processes of purification. It is barely possible that this latter supposition may account for it in the last case, where the strongest test for bromine was obtained, as this was acidified before distillation with steam, and hydrobromic acid produced by the sulphuric acid and sodic bromide might have converted some of the excess of benzyl alcohol into benzyl bromide, although this seems highly improbable, because the solution was kept throughout in a very dilute state. In the two previous cases, however, this explanation cannot apply, as no acid whatever had been added, so that no hydrobromic acid could have been formed; we are forced therefore to assume that the benzyl bromide was formed by the direct reaction and not by a secondary one, and under these circumstances the following reaction is the only one which seems to us admissible:



This is certainly very improbable, and we should add, that, when we tried to confirm it by a repetition of the experiment, we did not succeed in detecting any benzyl bromide in the product. At first sight it would seem that a reaction the reverse of that given above would be more probable, but we proved that this was not the case by a special experiment, which showed that benzyl bromide had no action on the sodium salt of trinitrophloroglucine under the conditions used by us. We may add that amyl bromide also has no action under these conditions. On the other hand, there is little doubt that the benzyl bromide, if formed by this reaction, would act on the sodic benzyolate forming benzyloether. Accordingly, we tried to isolate benzyloether from the oily product of the reaction by distilling off the excess of benzyl alcohol; there was so little of the residue which did not pass over at 207° that it was impossible to purify it properly; such as it was, however, it gave results on analysis agreeing with those calculated for benzyl alcohol (carbon 76.70 instead of 77.78). We conclude, therefore, that if the reaction given above takes place, it is only to a very moderate extent, the principal reaction being the formation of the trinitrophloroglucine tribenzyloether, which was then more or less saponified by the sodic hydrate

formed by the action of atmospheric moisture on the sodic benzyolate. We have not succeeded in detecting the organic substance formed by the removal of one or more nitro groups, as indicated by the appearance of sodic nitrite among the products.

Sodic Isobutylate or *Sodic Isoamylate* acted with tribromtrinitrobenzol in the same way as the alcoholates already mentioned, but the organic products insoluble in water were oily, and we did not succeed in isolating any compounds fit for analysis from them. The aqueous filtrates contained a considerable amount of the sodium salt of trinitrophenol. As the subject was not of sufficient interest to repay extended work, it was abandoned.

Quantitative Study of the Action of other Alcoholates on Tribromtrinitrobenzol.

The object of this work was to make a comparison between the actions of sodic ethylate and of other alcoholates on tribromtrinitrobenzol, and for this purpose we selected the quantitative determination of the amounts of sodic nitrite formed by the reaction, since our results with the ethylate had shown that the percentage of nitrogen removed as sodic nitrite was essentially constant under the conditions used by us. The amount of bromide formed was also determined in most cases, although of little value for purposes of comparison. Accordingly the following determinations were made, the results of which, with those from sodic ethylate already described, are given together in tabular form after the descriptions of the determinations. To economize our alcohols, as we had but a small stock of some of them, we have used principally the method with benzol as a solvent.

Experiments in which the Alcohol was the only Solvent.

XIV. Weight taken, 1.0578 gr. Alcoholate used, *sodic methylate*. Weight of aqueous solution, 115.1 gr. 54.3 gr. of the solution gave 13.6 c.c. of nitrogen from the sodic nitrite at a temperature of 18° and a pressure of 758.9 mm. 60.8 gr. of the solution gave 0.3768 gr. of argentic bromide.

XV. Weight taken, 1.157 gr. Alcoholate used, *sodic propylate*. Weight of aqueous solution, 92 gr. 54.1 gr. of this solution gave 13.8 c.c. of nitrogen from the sodic nitrite at a temperature of 16° and a pressure of 775.4 mm.

XVI. Weight taken, 1.1582 gr. Alcoholate used, *sodic isobutylate*. Weight of aqueous solution, 117.5 gr. 33.1 gr. of the solu-

tion gave 5.25 c.c. of nitrogen from the sodic nitrite at a temperature of 16° and a pressure of 765.5 mm. 43.3 gr. of the solution gave 0.2390 gr. of argentic bromide.

XVII. Weight taken, 1.2696 gr. Alcoholate used, *sodic isobutylate*. Weight of aqueous solution, 56.65 gr. 19.3 gr. of the solution gave 9.4 c.c. of nitrogen from the sodic nitrite at a temperature of 29°.5 and a pressure of 756.3 mm. 15.95 gr. of the solution gave 0.2198 gr. of argentic bromide.

XVIII. Weight taken, 1.5118 gr. Alcoholate used, *sodic isoamylate*. Weight of aqueous solution, 53.3 gr. 26.5 gr. of the solution gave 8.4 c.c. of nitrogen from the sodic nitrite at a temperature of 20° and a pressure of 762.4 mm. 26.25 gr. of the solution gave 0.3352 gr. of argentic bromide.

XIX. Weight taken, 1.5656 gr. Alcoholate used, *sodic isoamylate*. Weight of aqueous solution 85.1 gr. 37.4 gr. of the solution gave 9.9 c.c. of nitrogen from the sodic nitrite at a temperature of 19°.5 and a pressure of 766.2 mm.

Action of Sodic Methylate in Benzol.

XX. Weight taken, 1.0892 gr. Weight of solution, 65.7 gr. 31.7 gr. gave 10.1 c.c. of nitrogen from sodic nitrite at a temperature of 22° and a pressure of 766.9 mm. 34 gr. gave 0.4212 gr. of argentic bromide. The organic matter insoluble in water weighed 0.509 gr.

XXI. Weight taken, 1.2612 gr. Weight of aqueous solution, 40.05 gr. 17.35 gr. of the solution gave 11.7 c.c. of nitrogen from the sodic nitrite at a temperature of 25° and a pressure of 758.9 mm. 22.7 gr. of the solution gave 0.4088 gr. of argentic bromide.

XXII. Weight taken, 1.1561 gr. Weight of aqueous solution, 58.9 gr. 24.3 gr. of the solution gave 10.9 c.c. of nitrogen from the sodic nitrite at a temperature of 25°.5 and a pressure of 765.4 mm. 34.6 gr. of the solution gave 0.4732 gr. of argentic bromide.

Action of Normal Sodic Propylate in Benzol.

XXIII. Weight taken, 1.2281 gr. Weight of aqueous solution, 60.85 gr. 22.75 gr. of the solution gave 8.2 c.c. of nitrogen from the sodic nitrite at a temperature of 20°.5 and a pressure of 759.4 mm. 38.1 gr. of the solution gave 0.1398 gr. of argentic bromide.

XXIV. Weight taken, 1.297 gr. Weight of aqueous solution, 71.6 gr. 19.6 gr. of the solution gave 4.6 c.c. of nitrogen from the sodic nitrite at a temperature of 30° and a pressure of 767 mm. 52 gr. of the solution gave 0.7827 gr. of argentic bromide.

Action of Sodid Isopropylate in Benzol.

XXV. Weight taken, 1.3434 gr. Weight of aqueous solution, 50.15 gr. 20 gr. of the solution gave 5.9 c.c. of nitrogen from the sodic nitrite at a temperature of $24^{\circ}.5$ and a pressure of 762.5 mm. 30.15 gr. of the solution gave 0.2679 gr. of argentic bromide.

Action of Sodid Isobutylate in Benzol.

XXVI. Weight taken, 1.1598 gr. Weight of aqueous solution, 59.05 gr. 27.05 gr. of the solution gave 5.2 c.c. of nitrogen from the sodic nitrite at a temperature of $23^{\circ}.5$ and a pressure of 759.2 mm. 32 gr. of the solution gave 0.303 gr. of argentic bromide.

XXVII. Weight taken, 1.1551 gr. Weight of aqueous solution, 79.5 gr. 22.05 gr. of the solution gave 4.2 c.c. of nitrogen from the sodic nitrite at a temperature of 27° and a pressure of 764.5 mm. 57.45 gr. of the solution gave 0.722 gr. of argentic bromide.

Action of Sodid Isoamylate in Benzol.

XXVIII. Weight taken, 1.4427 gr. Weight of aqueous solution, 85.55 gr. 31.7 gr. of the solution gave 5.7 c.c. of nitrogen from the sodic nitrite at a temperature of 23° and a pressure of 760.9 mm. 40.65 gr. of the solution gave 0.4184 gr. of argentic bromide.

XXIX. Weight taken, 1.4485 gr. Weight of aqueous solution, 106.65 gr. 33.6 gr. of the solution gave 5.3 c.c. of nitrogen from the sodic nitrite at a temperature of $25^{\circ}.5$ and a pressure of 764.2 mm. 73.05 gr. of the solution gave 0.8515 gr. of argentic bromide.

Action of Sodid Benzylate in Benzol.

XXX. Weight taken, 1.0747 gr. Weight of aqueous solution, 92.2 gr. 33.5 gr. of the solution gave 2.7 c.c. of nitrogen from the sodic nitrite at a temperature of $30^{\circ}.5$ and a pressure of

758.8 mm. 58.7 gr. of the solution gave 0.5584 gr. of argentic bromide.

Action of Sodid Phenylate in Benzol.

XXXI. Weight taken, 1.1227 gr. Weight of aqueous solution, 67.15 gr. 32.5 gr. of the solution gave 3 c.c. of nitrogen from the sodic nitrite at a temperature of 29° and a pressure of 766.5 mm. 30.05 gr. of the solution gave 0.1568 gr. of argentic bromide.

The results of these experiments are collected in Tables III. and IV. with those previously given by sodic ethylate. The first column contains the sort of alcohol used and the number of the experiment, the second the weight of tribromtrinitrobenzol used, the third the percentage of nitrogen, and the fourth the percentage of bromine removed, calculated in the way already described in connection with Tables I. and II.

TABLE III.—EXPERIMENTS WITH THE ALCOHOL ALONE.

Sort of Alcohol used		Weight of Tribromtrinitro- benzol.	Percentage of Nitrogen	Percentage of Bromine.
Methyl	XIV.	1.0578	50.52	53.79
Ethyl	I.	10.556	45.88	42.53
	II.	10.1582	44.85	36.67
	III.	1.0306	46.95	42.85
	IV.	10.	46.86	39.39
	V.	10.	45.06	18.02
Propyl	XV.	1.157	38.80	-
Isobutyl	XVI.	1.1582	30.40	44.69
	XVII.	1.2696	37.85	49.04
Isoamyl	XVIII.	1.5118	20.62	36.16
	XIX.	1.5656	26.73	

TABLE IV.—EXPERIMENTS WITH ALCOHOL AND BENZOL.

Sort of Alcohol used.		Weight of Tribromtrinitro- benzol.	Percentage of Nitrogen.	Percentage of Bromine.
Methyl	XX.	1.089	35.28	59.62
	XXI.	1.261	38.37	45.64
	XXII.	1.156	41.17	55.59
Ethyl	VI.	10.022	33.58	59.54
	VII.	10.1976	33.09	38.91
	VIII.	1.2524	33.03	74.32
	IX.	1.2682	33.31	66.21
	X.	1.2287	34.42	49.10
Propyl	XXIII.	1.2281	32.74	14.51
	XXIV.	1.297	22.83	66.30
Isopropyl	XXV.	1.3434	19.87	26.46
Isobutyl	XXVI.	1.1598	17.68	38.46
	XXVII.	1.1551	23.41	69.01
	XXVIII.	1.4427	19.53	48.70
	XXIX.	1.4485	20.89	68.50
Benzyl	XXX.	1.0747	12.00	65.09
Phenyl	XXXI.	1.1227	9.78	24.90

An examination of Tables III. and IV. shows that the percentages of nitrogen obtained with the ethylate are the only ones which agree among themselves, the numbers with other alcoholates often differing by about six per cent, in one case by nearly ten per cent. Under these circumstances it is obviously unwise to attempt to draw any definite inferences from these results; we therefore dismiss them with the general remark that the amount of nitrogen removed seems to show a tendency to diminish as the molecular weight of the alcohol increases.

The length of time during which the mixture of tribromtrinitrobenzol and the alcoholate stood seemed to have but little influence on the reaction, as is shown by Experiments V., XXIV., XXVII.,

and XXIX., in which the mixture stood one or more days longer than the eighteen hours used for the other experiments. In fact, longer standing could not have any great effect in the case of the ethylate, as in eighteen hours eighty to ninety per cent of the tribromtrinitrobenzol had entered into the reactions. With the higher alcoholates this was not the case, and it may be that the action had not reached its end in eighteen hours, and that the variation observed in the percentages was due to differences in the times of reaction; but some experiments, in which the mixtures were allowed to stand a longer time in order to test this point, gave unsatisfactory results, apparently on account of the oxidation of the sodic nitrite formed by the oxygen of the air.

PART III.

ACTION OF SODIC ETHYLATE ON CERTAIN DERIVATIVES OF TRIBROMTRINITROBENZOL CONTAINING ALKYL OXY RADICALS.

Action of Sodic Ethylate on the Triphenylether of Trinitrophloroglucine.

This work was undertaken in the hope that the triphenylether of trinitrophloroglucine, $C_6(OC_6H_5)_3(NO_2)_3$, might behave toward sodic ethylate like tribromtrinitrobenzol, that is, lose one or more nitro groups as sodic nitrite, which would be replaced by the ethoxy group. This hope, however, has not been fulfilled, as instead of the nitro groups the phenoxy radicals are removed by the sodic ethylate, becoming replaced by ethoxy groups, while sodic phenylate is formed. The experiments were carried on as follows. 2.5 gr. of the triphenylether of trinitrophloroglucine* dissolved in benzol were mixed with the sodic ethylate from 0.4 gr. of sodium, and the bright red mixture allowed to stand two or more hours in the cold. After this it was allowed to evaporate spontaneously, and the residue warmed with water on the steam bath, when most of it dissolved. The insoluble portion was purified by crystallization from alcohol

* In preparing this substance from tribromtrinitrobenzol again we have found that a tolerable excess of sodic phenylate should be used in order to avoid the formation of a compound containing bromine, $C_6(OC_6H_5)_2Br(NO_2)_3$ probably. With such an excess, the reaction runs without heat, and is complete in a few minutes. We have not observed the green color noticed by us last year (these Proceedings, XXV. 188), which must therefore have been due to some impurity.

until it showed the constant melting point 119–120°, which indicated that it was trinitrophloroglucine triethylether, and this was proved to be the case by the following analysis:—

0.2080 gr. of the substance gave 22.5 c.c of nitrogen at a temperature of 21° and a pressure of 759.3 mm.

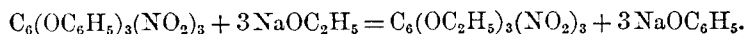
	Calculated for $C_6(OC_2H_5)_3(NO_2)_3$.	Found.*
Nitrogen	12.17	12.30

The aqueous filtrate which contained the other products of the reaction beside the trinitrophloroglucine triethylether gave no test for sodic nitrite, even with starch paste, potassic iodide, and sulphuric acid. It was acidified with dilute sulphuric acid and extracted with ether, which left an oily substance solidifying after some time, and smelling strongly of phenol. To prove that this was phenol, it was dissolved in a large quantity of water and bromine water added to the solution, which gave a white precipitate melting constant after crystallization from dilute alcohol at 92°, the melting point given by Post for tribromphenol; as however both Körner and Sinden give 95°, we thought it necessary to analyze the substance, which was done with the following result:—

0.2803 gr. of the substance gave according to the method of Carius 0.4748 gr. of argentic bromide.

	Calculated for $C_6H_3Br_3OH$.	Found.
Bromine	72.51	72.07

There can be no doubt, therefore, that the substance is tribromphenol, and that the action of the sodic ethylate upon trinitrophloroglucine triphenylether takes place according to the following reaction:



The bright red color observed in the solution was undoubtedly due to some of the sodium salt of trinitrophloroglucine formed by the action of the small amount of sodic hydrate, which it is almost impossible to exclude from sodic ethylate owing to the hygroscopic nature of absolute alcohol.

* This analysis has also been given earlier in this paper, where the composition of the triethylether is first determined.

This decomposition of the trinitrophloroglucine triphenylether by sodic ethylate calls to mind the behavior of esters with another alcohol and a small quantity of an alcoholate, as studied by Purdy* and Peters,† especially as our ether approaches the esters on account of the marked acid properties of the trinitrophloroglucine. Kossel and Krüger‡ have also found that sodic ethylate converts salol into salicylic ester (or acid), and sodic phenylate, and that glycerids are decomposed by sodic ethylate in a similar way, a result which is confirmed by Obermüller.§

Action of Sodic Ethylate on Tribromnitroresorcine Diethylether.

Early in our work with the tribromnitroresorcine diethylether melting at 101° we noticed that, although it was not acted on by a cold solution of sodic ethylate in alcohol, it was attacked if heated with such a solution, but our attempts to study this reaction were baffled for a long time by the difficulty in removing from the crystalline product the large amount of tarry matter which was formed at the same time, even constituting almost the whole of the mass, if the heat was not applied cautiously. After many experiments we succeeded in obtaining a satisfactory result by proceeding as follows. 13 gr. of tribromnitroresorcine diethylether were covered with absolute alcohol, and an alcoholic solution of sodic ethylate added. The flask containing the mixture was, after fitting it to a return condenser, immersed in a beaker of cold water, which was heated slowly. As the temperature rose the substance went into solution with a pale reddish color, and in a few minutes after that there was a sudden change, the solution becoming almost black, although the reaction was not at all violent. At this point the heating must be stopped to avoid the formation of a large quantity of the tarry impurity. The contents of the flask, which had a peculiar aromatic odor not belonging to the compound we have isolated, was allowed to evaporate to dryness spontaneously, and the residue washed several times with cold water, which was found to contain sodic bromide. The water left undissolved a most unpromising tarry mass with almost no sign of crystalline form, but by extracting it with hot ligroine a crystalline substance was obtained, which was purified by repeated crystallization from hot alcohol with the aid of

* Ber. d. ch. Ges., XX. 1554.

† Zeitschr. Physiol. Chem., XV. 321.

‡ Ann. Chem., CCLVII. 353.

§ Ibid., XVI. 152.

bone-black until it melted constant at 115° , when it was dried at 100° and analyzed with the following results:—

- I. 0.1897 gr. of the substance gave on combustion 0.2874 gr. of carbonic dioxide and 0.0782 gr. of water.
- II. 0.1519 gr. of the substance gave according to the method of Carius 0.0985 gr. of argentic bromide.

	Calculated for $C_6H_2BrNO_2(OC_2H_5)_2$.	Found.	
		I.	II.
Carbon	41.38	41.31	
Hydrogen	4.14	4.58	
Bromine	27.58		27.60

The substance has therefore been formed from the tribromnitroresorcine diethylether by the replacement of two atoms of bromine by two of hydrogen, a reaction which is similar in principle to the replacement of the bromine by hydrogen in bromdinitroresorcine diethylether, when treated with a boiling solution of sodic ethylate in alcohol, and to the similar replacements of bromine by hydrogen in the formation of bromdinitrophenylmalonic ester and related substances from tribromdinitrobenzol and tribromtrinitrobenzol.

Properties of Bromnitroresorcine Diethylether,
 $C_6H_2BrNO_2(OC_2H_5)_2$.

The substance crystallizes from hot alcohol in long radiating silky white needles, which melt at 115° , and are soluble in cold alcohol, more freely in hot; freely soluble in cold methyl alcohol; very freely in benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in cold ligroine, much more soluble in hot; essentially insoluble in water. Neither hydrochloric, nitric, nor sulphuric acid seems to have any action on it, and the same is the case with a solution of sodic hydrate.

XXII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

ON THE ACTION OF WATER UPON TRIBROMTRINITROBENZOL AND TRIBROMDINITROBENZOL.*

BY C. LORING JACKSON AND W. H. WARREN.

Presented June 15, 1892.

IN an article † recently published, C. A. Lobry de Bruyn describes the action of an aqueous solution of sodic carbonate upon the unsymmetrical trinitrobenzol (1, 2, 4) which produces the dinitrophenol (OH, 1, 2, 4) by the replacement of a nitro group by hydroxyl. After we had shown in an earlier paper ‡ that the nitro groups can be removed from tribromtrinitrobenzol by sodic alcoholates, M. Lobry de Bruyn suggested to us in the most courteous way that it would be interesting to see whether an aqueous solution of sodic carbonate would not have a similar effect on this substance, which seemed not improbable after his work already cited. The following paper contains an account of the work we undertook in accordance with this suggestion, the results of which can be briefly summarized as follows. Symmetrical tribromtrinitrobenzol (melting point 285°) is converted by boiling with sodic carbonate and water into a mixture of the sodium salts of trinitrophenol and a tribromdinitrophenol, $C_6Br_3(NO_2)_2OH$, melting at 194° , which, so far as we can find, has not been described as yet. Tribromdinitrobenzol (melting point 192° , made from symmetrical tribrombenzol) gave under the same conditions a dibromdinitrophenol which melts at $147-148^{\circ}$, a melting point almost identical with that of the only other dibromdinitrophenol known ($146^{\circ}-146.5^{\circ}$),

* The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by W. H. Warren.

† Rec. Trav. Chem., IX. 185.

‡ These Proceedings, XXV. 164.