

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

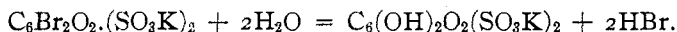
CERTAIN DERIVATIVES OF TETRABROMO-*o*-QUINONE.¹

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This paper contains an account of our study of the behavior of tetrabromo-*o*-quinone with dipotassium sulfide, and with dimethylamine.

When a solution of tetrabromo-*o*-quinone in benzene is shaken with aqueous dipotassium sulfide, the principal product is potassium dibromopyrocatechindisulfonate, $C_6Br_2(OH)_2(SO_3K)_2$, from which we prepared the barium salt $C_6Br_2(OH)_2(SO_3)_2Ba \cdot 3H_2O$, and the calcium salt $C_6Br_2(OH)_2(SO_3)_2Ca \cdot 4H_2O$. If this potassium salt was moistened with strong nitric acid with careful cooling, a red product was obtained, which we think is potassium dibromo-*o*-quinonedisulfonate, $C_6Br_2O_2(SO_3K)_2$, contaminated with a little potassium nitrate, which we were unable to remove. This substance dissolved in cold water, a little less than a gram being taken up by 1 cc. of water; but, if the solution stood overnight at ordinary temperatures, it deposited much less soluble red crystals of the tripotassium euthiochronate, which was identified by conversion into the tetrapotassium salt, when the characteristic change of color with analyses of this latter salt left no doubt about the nature of the substance.



After this reaction had taken place the dioxyorthoquinone would at once change to the more stable *p*-quinone (euthiochronic acid) according to all the observations of similar cases. The euthiochronate was also formed by the action of potassium hydroxide solution.

Our reasons for believing that the immediate product from the action of nitric acid contains an orthoquinone group are: its red color, the ease with which water converts it into a euthiochronate, and the extreme activity of the atoms of bromine in it, since they are removed from it by water at ordinary temperatures, whereas the original potassium dibromopyrocatechindisulfonate gave up no bromine even to boiling water, and with a solution of potassium hydroxide it was necessary to heat in order to form the euthiochronate. That the orthoquinone group has a very vigorous action in loosening halogen atoms associated with it has been shown by all our experience. The objection that the red color of our product may be caused by the presence of tripotassium euthiochronate is met by the observation that the solution of our salt deposits crystals of the euthiochronate on standing for some hours, so that it must be less soluble than our product, and seems to be formed from it gradually by the action of water.

¹ 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 Sydney Adams Beggs.

As it seemed probable that so negative an *o*-quinone as the potassium dibromo-*o*-quinonedisulfonate would behave like tetrabromo-*o*-quinone, we tried some experiments in the hope of obtaining α -addition compounds¹ from it; but after six months no action could be observed with ethyl, or benzyl alcohol, and although methyl alcohol gave a white product, its amount was too small to determine its nature.

The potassium dibromo-*o*-quinonedisulfonate, when made with nitric acid, contained an impurity of niter, as already mentioned. In the hope of obtaining it free from impurity we exposed potassium dibromopyrocatechindisulfonate to electrolytic oxidation, but although the quinone salt was formed, as shown by the red color, we could not obtain it in this way, since by the time the pyrocatechin salt was completely oxidized the greater part of the red quinone salt had been destroyed, showing that it is as susceptible to oxidation as its mother substance. If the action was continued, till the red color had gone, most of the organic matter seemed to have been burnt up, but a small yield of pentabromoacetone was obtained. This was recognized by bromine and molecular weight determinations, which were necessary, as we found its melting point 73–74° (uncorr.), whereas it is given by Beilstein as 76°. In a research on hexabromodiacetyl² Adams and one of us also encountered pentabromoacetone, and entirely independently found its melting point 73° (uncorr.). An examination of the work of others on this subject shows that we are not alone in this experience, Wilde³ giving 71–72°, Wichelhaus⁴ 74°, Steiner⁵ 74°, while the higher melting points were obtained by Benedikt⁶ 76°, and Zincke and Kegel⁷ 76–77°. The explanation of these discrepancies is probably to be found in the observation of Benedikt that the alcoholic solution of pentabromoacetone, although neutral at first, in a few hours becomes acid and smells of bromoform. In all the cases with lower melting points the crystallization was carried on in alcohol, and enough impurity may have been formed to lower the melting point, although it did not show in the analyses in any case except Steiner's, whose product was so impure that the analyses misled him at first in regard to its nature.⁸ The highest result—that of Zincke and Kegel—was obtained after crystallization from ether and benzene. Benedikt speaks of crystallizing from alcohol or chloroform. If our explanation is correct his melting point was probably taken after the use of the latter.

¹ Jackson and Porter, *Am. Chem. J.*, 31, 89 (1904).

² THIS JOURNAL, 37, 2532 (1915).

³ *Ann.*, 127, 167 (1863).

⁴ *Ibid.*, 152, 260 (1869).

⁵ *Ber.*, 7, 505 (1874).

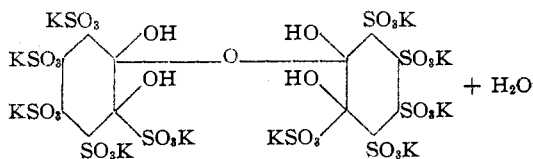
⁶ *Ann.*, 189, 168 (1878).

⁷ *Ber.*, 23, 1725 (1890).

⁸ Steiner, *Ibid.*, 7, 1284 (1874).

As already stated, when a solution of dipotassium sulfite was shaken with a benzene solution of tetrabromo-*o*-quinone, the product was potassium dibromopyrocatechindisulfonate, but with this there was formed a small quantity of another white salt, which could be made the principal product of the reaction by heating the solution of the dipotassium sulfite to 50° before shaking it with the benzene solution of tetrabromo-*o*-quinone instead of carrying on the reaction in the cold. In this connection we had the strange experience of finding we could not prepare this new salt for nearly a year, the potassium dibromopyrocatechindisulfonate being the only product obtained under conditions which both before and after it gave the new compound invariably. In spite of a careful study we are able to give no explanation of this phenomenon.

The complete analysis of this compound led to the formula $C_6(SO_3K)_5O_3H_3$, or some multiple of it, which would make it the *o*-thiochronate retaining like the corresponding para compound one molecule of water at 130° (4 molecules of water were lost below 130° leaving the formula given above). We cannot, however, accept this view of its constitution for the following reasons: The *p*-thiochronate has a distinct yellow color, and in view of the fact that *o*-quinones are more highly colored than *p*-quinones, the *o*-thiochronate should be red, but the new compound is white. The thiochronate is easily converted into a euthiochronate by potassium hydroxide; the new compound can be boiled with a strong solution of this reagent without change. Hydrochloric acid also reacts with the thiochronate, when boiled with it, but the new compound is unaffected by it below 150°, at which temperature it is completely charred. The thiochronate gives an intense brown-red color with ferric chloride; the new compound barely deepens the yellow color of the reagent and it does not reduce a solution of a silver salt, whereas the thiochronate does. The α -water addition compound¹ of the *o*-thiochronate containing one molecule of water of crystallization should have all the



properties enumerated above except the indifference to boiling hydrochloric acid, since the water compound of tetrabromo-*o*-quinone is affected by this reagent, but as the action consists in the formation of chlorine, and therefore is evidently due to the free carbonyl in the bromine compound, which does not exist in our salt, the difference does not tell strongly against our formula. Further, such a derivative would be expected from

¹ Jackson and Porter, *Am. Chem. J.*, 31, 109 (1904); Jackson and MacLaurin, *Ibid.*, 37, 87 (1907).

the *o*-thiochronate, if this were the first product of the reaction, as the molecule is highly charged with negative radicals, which, so far as is known, favor the formation of these addition compounds. As already stated it is necessary to assume the presence of a molecule of water even at 130°, but this does not tell against our formula, as Graebe¹ found that the thiochronate also retains a molecule of water at such high temperatures. We have adopted provisionally this formula for the substance for the reasons given above, but it must be remembered that it cannot be finally accepted, until it has been confirmed by additional experiments.

As aniline gave a number of well-marked derivatives² with tetrabromo-*o*-quinone, we thought that equally good results might be obtained by the action of secondary amines, but our experiments in this direction were disappointing. Methylaniline gave only a tar, although we tried a great many conditions of temperature solvents and proportions; and from dimethylamine we obtained only one product in unstable black crystals, thrown down when it was passed into a solution of tetrabromo-*o*-quinone. Its formula is probably $C_6Br_4O_2(NH(CH_3)_2)_2$. The tetrachloro-*o*-quinone gave a corresponding product. They seem to belong with the similar addition compounds sometimes classed with the quinhydrones.

Experimental.

Action of Dipotassium Sulfito on Tetrabromo-*o*-quinone in the Cold. Dibromopyrocatechindisulfonic Acid.—The dipotassium sulfito used in this work was prepared by dissolving 112 g. of potassium hydroxide in 100 cc. of water, and passing into the solution the sulfur dioxide obtained from 120 g. of acid sodium sulfito with dilute sulfuric acid. Care must be taken that none of the sodium salt spatters over into the potassium salt solution. Upon diluting to 316 cc. a solution was obtained, 2 cc. of which contained 1 g. of K_2SO_3 .

Fifty-six cc. of this solution diluted to 100 cc. were placed in a 250 cc. Erlenmeyer flask, and, after cooling with ice to about 10°, 10 g. of tetrabromo-*o*-quinone dissolved in 60 cc. of benzene were added, the two liquids thoroughly shaken together, and immediately filtered to remove a small amount of white scum that formed at the surface of contact. In the filtrate it was observed that the red color had been transferred from the benzene to the aqueous liquid showing that a reaction had taken place, but on standing for 15 to 30 minutes this red color gradually disappeared from the sulfito solution also, and crystals were deposited, the amount of which increased on standing overnight. These white needles were purified by crystallization from water. Some drying experiments showed that the salt was free from water of crystallization. It was dried at 120° for analysis.

¹ *Ann.*, 146, 40 (1868).

² Jackson and Porter, *Am. Chem. J.*, 30, 518 (1903).

Subs., 0.1422, 0.1777, 0.1794; AgBr, 0.1036; K_2SO_4 , 0.0611; $BaSO_4$, 0.1629 by the method of Carius.

Calc. for $C_6Br_2(OH)_2(SO_3K)_2$: Br, 31.75, K, 15.52, S, 12.70. Found: Br, 31.00, K 15.44, S 12.47.

The substance is therefore potassium dibromopyrocatechindisulfonate.

Properties.—It crystallizes in clusters of white needles, easily soluble in hot water, less so in cold; insoluble in alcohol, or ether. Lead acetate throws down from its solution a white lead salt, which is slightly soluble in water, but as this undoubtedly contained basic salt, it was not analyzed. Silver nitrate is reduced by it on standing. Ferric chloride gives a deep blue color with it. A hot solution of potassium hydroxide turns it dark brown, and converts it after boiling for two hours into potassium euthiochronate, recognized by its characteristic color reactions.

Barium Dibromopyrocatechindisulfonate, $C_6Br_2(OH)_2(SO_3)_2Ba \cdot 3H_2O$.—It was a matter of some difficulty to obtain this salt free from potassium. The lead salt precipitated with lead acetate from a hot concentrated solution of the potassium salt was so gelatinous that a considerable amount of potassium acetate was retained by it, and this was only partially removed by boiling the precipitate 3 or 4 times with small quantities of water, and these boilings could not be continued beyond this on account of the solubility of the lead salt in hot water, which, however, was not great enough to permit its purification by crystallization.

At last we proceeded as follows: The lead salt made and partially freed from potassium acetate as described in the last paragraph was mixed with a little cold water, and treated with a slight excess of dilute sulfuric acid. After the mixture had stood for some time with occasional stirring, the lead sulfate was filtered off, and the filtrate shaken with barium carbonate. It was then warmed on the steam bath to complete the reaction and drive off the carbon dioxide, and the filtrate was evaporated to dryness, after which it was crystallized once from hot water, when it was found by the flame test that the impurity of potassium salt had been removed.

Subs., air dried, 0.3094, 0.2288, 0.3090. Loss at 110° , 0.0277, 0.0198, 0.0268. Subs. dried at 110° , 0.2835, 0.2815; $BaSO_4$, 0.1174, 0.1142.

Calc. for $C_6Br_2(OH)_2(SO_3)_2Ba \cdot 3H_2O$: H_2O , 8.75. Found: H_2O , 8.95, 8.66, 8.67.

Calc. for $C_6Br_2(OH)_2(SO_3)_2Ba$: Ba, 24.39. Found: Ba, 24.32, 23.85.

It is a white, crystalline salt, more soluble in hot water than in cold; insoluble in alcohol.

Calcium Dibromopyrocatechindisulfonate, $C_6Br_2(OH)_2(SO_3)_2Ca \cdot 4H_2O$.—This substance was made in the same way as the barium salt except that the purified lead salt was treated with an amount of dilute sulfuric acid insufficient to act on all the lead. The filtrate, after a small portion had shown the absence of sulfuric acid by the usual test, was treated with calcium carbonate, and purified in the same way as the barium salt.

Subs., air dried, 0.4467, 0.3005. Loss at 120°, 0.0569, 0.0384.

Calc. for $C_6Br_2(OH)_2(SO_3)_2Ca \cdot 4H_2O$: H_2O , 13.39. Found: H_2O , 12.74, 12.78.

Subs. dried at 120°, 0.2352; $CaSO_4$, 0.0676.

Calc. for $C_6Br_2(OH)_2(SO_3)_2Ca$: Ca, 8.59. Found: Ca, 8.45.

It is a white crystalline solid, easily soluble in water; insoluble in alcohol.

Our attempts to prepare dibromopyrocatechindisulfonic acid failed because of the instability of the acid. The solution obtained from the lead salt with insufficient sulfuric acid turned red, even when evaporated at ordinary temperatures whether spontaneously, or by means of a blast of air, and although the residue was white, it evidently was not a sulfo-acid, and could be obtained only in very small quantity. Sulfuretted hydrogen even on long standing gave only a slight decomposition of the lead salt, and we did not succeed in freeing the filtrate from colloidal lead sulfide.

Action of Nitric Acid on Potassium Dibromopyrocatechindisulfonate.—

Five grams of the finely pulverized salt were thoroughly cooled in a glass dish immersed in ice, and moistened with strong nitric acid, when the appearance of a red color showed that a reaction had taken place. To complete this the mixture was allowed to stand for some time in the ice, as at ordinary temperatures the first product is decomposed. When the mass became stiff and pasty, it was ground with a pestle to bring the acid into contact with the salt as completely as possible; and when in spite of the cooling red nitrous fumes began to come off rapidly, the action was stopped by the addition of alcohol, and afterward the mass was washed thoroughly with alcohol. We could find no method of freeing this substance from an impurity of potassium nitrate, as the only solvent for it was water, and this decomposed it even in the cold.

On one occasion a specimen was obtained, which gave a percentage of potassium only about 1% higher than that required by potassium dibromo-*o*-quinonedisulfonate, $C_6Br_2O_2(SO_3K)_2$, and this specimen contained an impurity of niter, as was shown by the diphenylamine test. About 4 g. of the crude red salt were obtained from 5 g. of the pyrocatechin salt. Our reasons for considering this product a quinone are given in the introduction.

The greater part of 5 g. of the red salt dissolved in 5 cc. of cold water, but if the filtered solution was allowed to stand overnight, it deposited red crystals, which were obviously different from the quinone salt, as they were so much less soluble. In one experiment these crystals weighed 0.8 g., and 0.7 g. in addition was obtained by evaporating the filtrate to half the original volume; but further evaporation gave only a tarry residue. This new red salt was free from bromine, and was recognized as tripotassium euthiochronate by the addition of potassium hydroxide, which converted it into the yellow tetrapotassium salt, and this gave the following results on analysis:

Calc. for $C_6O_2(OK)_2(SO_3K)_2H_2O$: H_2O , 3.86. Found: H_2O , 4.25, 4.46.

Calc. for $C_6O_2(OK)_2(SO_3K)_2$: K, 34.57. Found: K, 34.60.

Our analyses of the tripotassium salt gave unsatisfactory results, apparently from the formation of some tetrapotassium salt during its attempted purification by crystallization from water.

Specimens of the crude potassium dibromo-*o*-quinonedisulfonate were allowed to stand with methyl, ethyl, and benzyl alcohols in the hope of obtaining α - or β -addition compounds similar to those obtained from tetrabromo-*o*-quinone,¹ and after 6 months it was found that a white crust had formed on the surface of the specimen with methyl alcohol, but no action was visible in the other two experiments. This may have been the desired α -addition compound, but the amount was too small for us to determine its nature. Owing to the insolubility of the salt in alcohol such a sluggish action would be expected here, but we could devise no way of hastening it, since the salt is decomposed by water, in which alone it is soluble.

Electrolytic Oxidation of Potassium Dibromopyrocatechindisulfonate.

—This work was undertaken in the hope of preparing the orthoquinone salt in a state of purity. Five grams of the dibromopyrocatechindisulfonate were dissolved in 125 cc. of water, and put in a porous cup surrounded by the same solution. The anode, a square piece of platinum foil, was immersed in the cup, and a current of about 0.8 ampere was passed through the solution, which turned red, indicating the formation of the *o*-quinone salt, but we did not succeed in isolating it, because tests showed the presence of the pyrocatechin salt also, and owing to the easy decomposition of the quinone salt it could be obtained pure only as the direct product of the reaction, any attempt to crystallize it from water converting it into the euthiochronate. As the pyrocatechin salt disappeared from the solution, the red color also vanished, and after passing the current for 24 hours the only product we could find was a white solid insoluble in water. Most of the salt seemed to have been burnt up, however, as the average yield of the white product was 0.15–0.3 g. from 5 g. of the salt. This substance, which contained no sulfur, was crystallized from dilute alcohol, until it showed the constant melting point 73–74° (uncorr.), when it was proved to be pentabromoacetone by the following determinations:

Calc. for CBr_5COCBr_2H : Br, 88.31; M. W., 453. Found: Br, 88.51, 88.76; M. W., 444, 412.

The reason for our low melting point (73–74° instead of 76°) has been considered in the introduction.

Action of a Warm Solution of Dipotassium Sulfite on Tetrabromo-*o*-quinone.—When tetrabromo-*o*-quinone was treated with a cold solution

¹ Jackson and Porter, *Am. Chem. J.*, 31, 89 (1904).

of dipotassium sulfite, the principal product was potassium dibromopyrocatechindisulfonate as already described, but in addition to this there was also formed a minute amount of another substance crystallizing in white plates, which differed from the principal product in that it gave an insoluble barium salt, and remained colorless with ferric chloride (instead of turning blue), and with nitric acid (instead of giving a red color). By carrying on the reaction at a higher temperature this new compound became its principal product. 28 g. of dipotassium sulfite dissolved in 100 cc. of water were heated to 50°, and shaken with 10 g. of tetrabromo-*o*-quinone dissolved in 60 cc. of benzene. The red color was transferred from the benzene to the aqueous solution, but on standing overnight it disappeared entirely, and white crystals were deposited. The strength of the sulfite solution does not affect the product, the same compound being obtained with 200 cc. or 56 cc. of water. 50 g. of tetrabromo-*o*-quinone yielded about 35 g. of the crude product.

Our experience with this preparation was very strange. We tried it first in the spring of 1912, and in the autumn of the same year we studied the effect of different conditions of temperature and concentration on the process, and found that by varying the temperature we could prepare at will either the new substance, or potassium dibromopyrocatechindisulfonate. We accordingly used our supply of the new compound freely, but when in December we tried to make more of it, we could get nothing but potassium dibromopyrocatechindisulfonate under conditions which had given the white substance in quantity in our earlier work. We next made a careful study of all the conditions of the reaction, but no changes in the temperature, concentration of the solutions, or nature of the preparations of the tetrabromopyrocatechin or dipotassium sulfite led to the desired result. In every case the product was the potassium dibromopyrocatechindisulfonate. In the autumn of 1913, however, we repeated the preparation, and then obtained the new compound again without difficulty by the method described above. The only differences we could find between the experiments that gave the substance and those which did not were that they were carried on in the autumn instead of in December and the following months, and in a different room in the same building in the later cases. More work is necessary to explain this interesting experience, but we think the explanation will not be found in any slight variations of the conditions of the process, as our careful study of these led to no result.

The process began to yield the new substance again, after our work together had come so nearly to an end that our investigation of it is of necessity somewhat meager. It was purified by 3 crystallizations from hot water, when it was found to combine no bromine.

Subs., 0.3664, 0.3420. Loss at 120°, 0.0361, 0.333.

Calc. for $C_{12}H_8S_{10}K_{10}O_{30} \cdot 8H_2O$: H_2O , 9.11. Found: H_2O , 9.85, 9.74.

Subs. dried at 120°, 0.3340, 0.3318, 0.1325, 0.1048, 0.1666, 0.1921, 0.1974; CO_2 , 0.1271, 0.1248; H_2O , 0.0199, 0.0227; $BaSO_4$, 0.2014, 0.1606, 0.2605; K_2SO_4 , 0.1156, 0.1169.

Calc. for $C_{12}H_8S_{10}K_{10}O_{30}$: C, 10.03, H, 0.42, S, 22.28, K, 27.20. Found: C, 10.40, 10.26, H, 0.66, 0.76, S, 20.87, 21.00, 21.47, K, 27.02, 26.59.

These determinations of sulfur leave much to be desired, and this is undoubtedly due to the great difficulty with which the compound is decomposed in the Carius tube. If the heating was carried on for but one night as usual, only about 18% of S was found. To get the results given above it was necessary to heat the tubes for 36 hours, and it may well be that even then a portion of the substance had escaped decomposition. Reasons have been given in the introduction for thinking that this is the α -water addition product of potassium *o*-euthiochronate containing one molecule of water, perhaps of crystallization, $[C_6(SO_3K)_5(OH)_2]_2 \cdot O \cdot H_2O$.

Properties.—It forms white plates, slightly soluble in cold, freely in hot water, from which it crystallizes finely, insoluble in alcohol. Strong nitric acid has no apparent action on it. Barium chloride gives with its solution a white precipitate, which is soluble in hydrochloric acid. Silver nitrate, or lead acetate also gives a white precipitate. With the small amount of material at our disposal we did not succeed in obtaining any of these precipitates free from potassium. Ferric chloride gives with a solution of the salt a yellow color somewhat darker than its own. An attempt to make the sulfochloride was unsuccessful. Heating the salt with hydrochloric acid in a sealed tube gave no action below 150°, and at this temperature the substance was charred completely. Sodium hydroxide had no action on the salt, even when a strong solution was boiled with it.

Action of Dimethylamine on Tetrabromo-*o*-quinone.—Five grams of tetra-bromo-*o*-quinone were dissolved in 50 cc. of ether, and after cooling the solution with ice, dimethylamine was passed into it, as long as black crystals separated. The same result was obtained when alcohol, or chloroform, was used as the solvent. The black product was recrystallized from benzene, or chloroform, and dried rapidly *in vacuo*.

Calc. for $C_6Br_4O_2(NH(CH_3)_2)_2$: Br, 62.24. Found: Br, 62.88, 63.40.

These results—the best we obtained—are as good as could be expected, because the substance decomposes on solution forming a red product, and giving off the odor of dimethylamine, and it is also converted into a tar by standing dry for some time even *in vacuo*.

Properties.—Black crystals, which decompose between 115° and 125°, the temperature being so much affected by the conditions of heating that no definite point can be given. On standing in the air or over sulfuric acid it is converted into a tar—a change which takes place rapidly, if the substance has not been washed and recrystallized, and goes on slowly

even under the most favorable conditions. It is soluble in alcohol, acetone, chloroform, benzene, or toluene; slightly soluble in ether; essentially insoluble in water, or naphtha. The solution of the compound is always attended with decomposition shown by the appearance of a red substance and of a tar if the solution is allowed to stand for some time.

Similar black crystals were obtained, when alcoholic solutions of dimethylamine and tetrachloro-*o*-quinone were mixed after having been cooled with ice. An analysis after washing with water gave 39.50% Cl instead of the 42.27% Cl required, if one molecule of the quinone had combined with two of the amine. Owing to the instability of the substance, which prevented purification, a better result could not be expected. On standing dry or being dissolved with a view to purifying, it was converted into a tar, and it decomposed on heating. It seems, therefore, to be a little less stable even than the corresponding bromine compound, and is less soluble than this, since it is only slightly soluble in alcohol, or acetone, and nearly insoluble in chloroform, tetrachloride of carbon, disulfide of carbon, benzene, or toluene, but soluble in ether.

CAMBRIDGE, MASS

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

NOTE ON TETRABROMO-*o*-PHENYLENEDIACETAMID.

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In some earlier work² in this laboratory an attempt was made to prepare tetrabromo-*o*-phenylenediamine by the action of bromine on the free base, but the only products were amorphous red substances, which were supposed to be formed by the action of bromine on the amino groups. Accordingly in taking up the work again we protected these groups by the introduction of acetyl, and had no difficulty in obtaining tetrabromo-*o*-phenylenediacetamid (not melting below 280°) by the direct action of bromine on dibromo-*o*-phenylenediacetamid. When we attempted to remove the acetyls from this substance with sulfuric acid, we found that a molecule of water was removed instead. This was not unexpected, but we had hoped that some other saponifying agent might be found, which would yield the free diamine. With this end in view we tried a solution of sodium hydroxide in an open vessel, and alcoholic ammonia in a sealed tube, but each gave the same result as the sulfuric acid, that is, a compound melting at 265–266° (uncorr.), which without doubt is the acet

¹ 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 Sydney Adams Beggs.

² Jackson, Russe, *Am. Chem. J.*, 35, 148 (1906).