they must have a lining of silicious material, owing to the readiness with which carbon is absorbed by the molten material.

The analysis of the product requires a special study of methods. This has been carried out with fairly satisfactory results. The composition of a representative sample was found as shown in the preceding table.

No determination thus far has been made for carbon, boron or titanium.

URBANA, ILLINOIS.

A CORRECTION.

In an article entitled, "Can the Dissociation Theory be Applied to Solid Solutions in Steels?" which appeared in the September number of THIS JOURNAL, the specific resistances of the steel which had been hardened and subsequently reheated to different temperatures were given. In order to render the values as near the absolute value as possible corrections to the observed values necessitated through the calibrations of the recording instruments were made. The corrections expressed in microhms due to the high reading of the ammeter used amount in the present case to from 0.21 to 0.24 microhms, according to the specific resistance. As the ammeter read too high these corrections should have been subtracted from the observed values, but by mistake the corrections were in all cases added. In order, therefore, to reduce the values reported to their true value, from 0.42 to 0.48 microhms should be subtracted from the figures given in the table. This correction would in no way affect the significance of the results or any deductions drawn therefrom.

E. D. CAMPBELL.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

HEXABROMODIACETYL.

BY C. LORING JACKSON AND ROGER ADAMS.

Received August 28, 1915.

In an earlier paper[1] A. H. Fiske and one of us described two acids, one melting at 207°, the other at 174°, made by the action of sodium hydroxide on tetrabromo-*o*-quinone, and it was also stated that, when treated with bromine and water, these acids were converted into a yellow diketone, to which the formula $CBr_3CHBrCOCOCBr_3$ was assigned. On continuing the study of this compound we have found that this formula is not the true one, but that it is really the hexabromodiacetyl $CBr_3COCOCBr_3$. The data on which this conclusion rests are given in Table I containing all the analytical results obtained by us from the substance itself and its principal derivatives. The first column gives the percentages calculated for $CBr_3CHBrCOCOCBr_3$, the second the data obtained by

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[1] *Am. Chem. J.*, 50, 341 (1913).

Dr. Fiske in the earlier part of the work, the third those obtained in the work described in this paper, and the fourth the percentages calculated for $CBr_3COCOCBr_3$.

TABLE I.

	1. $CBr_3CHBrCOCOCBr_3$.	2. Fiske.	3. Adams.	4. $CBr_3COCOCBr_3$.
Br	85.90	85.78; 86.00	85.88	85.70
C	9.20	9.84; 9.47	8.62	8.57
H	0.15	0.58; 0.50	0.40	0.0
MW	653	....	514; 512[1]	560
	Methyl Alcohol Addition.			
	$CBr_3CHBrCOC(OHOCH_3)CBr_3$.			$CBr_3COC(OHOCH_3)CBr_3$.
Br	81.75	81.21; 81.32	81.17; 81.01; 81.27[2]	81.08
C	10.51	10.52	10.26	10.14
H	0.73	0.97	0.86	0.68
MW	685	....	584; 588; 601[3]	592
	Ethyl Alcohol Addition.			
	$CBr_3CHBrCOC(OHOC_2H_5)CBr_3$.			$CBr_3COC(OHOC_2H_5)CBr_3$.
Br	80.11	80.17; 79.75	79.30; 79.11;[3] 79.52	79.20
C	12.01	12.35	12.01; 11.99	11.88
H	1.00	1.25	1.12; 1.09	0.99
MW	699	....	597; 582	606
	Benzyl Alcohol Derivative.			
	$CHBr_2CHBrCOC(OHOC_7H_7)CBr_3$.			$CHBr_2COC(OHOC_7H_7)CBr_3$.
Br	70.48	67.89; 68.29	68.01[4]	67.92
C	21.12	22.58	22.43	22.42
H	1.32	1.90	1.77	1.53
MW	681	....	580; 575; 577	589
	Acetone Reductions.			
	$CHBr_2CHBrCOCOCHBr_2$.			$CHBr_2COCOCHBr_2$.
Br	80.81	....	79.68; 79.80; 79.58[5]	79.60
MW	495	....	375; 383	402
	$CHBr_2CHBrCOC(OHOC_2H_5)CBr_3$.			$CHBr_2COC(OHOC_2H_5)CBr_3$.
Br	77.41	....	76.02; 76.43[6]	75.91
C	13.55	....	13.86	13.67
H	1.29	....	1.54	1.32
MW	620	....	502	527

[1] Subs. 0.7705, 1.3457, Δ 0.57, 1.0, C_6H_6 12.874. Subs. 0.3010, 0.2348, AgBr 0.6074, CO_2 0.0742, H_2O 0.084.

[2] Subs. 0.1483, 0.1987, 0.2394, 0.3090, AgBr 0.2829, 0.3783, 0.4571, CO_2 0.1162, H_2O 0.0241. Subs. 0.2151, 0.4482, 0.6655, Δ 0.15, 0.31, 0.45, C_6H_6 12.290.

[3] Subs. 0.1515, 0.1449, 0.1210, 0.2324, 0.2523, 0.2256, 0.5057, AgBr 0.2823, 0.2693, 0.2261, CO_2 0.1024, 0.1110, H_2O 0.0235, 0.0248, Δ 0.15, 0.345, C_6H_6 12.580.

[4] Subs. 0.1602, 0.2457, 0.2292, 0.4267, 0.7335, AgBr 0.2560, CO_2 0.2021, H_2O 0.0393, Δ 0.165, 0.31, 0.53, C_6H_6 11.971.

[5] Subs. 0.1918, 0.1529, 0.1271, 0.2465, 0.6717, AgBr 0.3591, 0.2866, 0.2381, Δ 0.27, 0.72, C_6H_6 12.164.

[6] Subs. 0.1427, 0.1416, 0.2230, 0.1850, AgBr 0.2549, 0.2543, CO_2 0.1133, H_2O 0.0309, Δ 0.135, C_6H_6 13.639.

This table brings to light the astonishing fact that the percentages calculated for the two formulas of the diketone and its methyl and ethyl hemiacetals differ by less than 1%, so that it is impossible to distinguish between them by these analyses, and further that the data at hand, when the earlier paper was written, justified the adoption of the heptabromomethyldiacetyl formula instead of that of the hexabromodiacetyl, since the results from the benzyl compound, which alone told against it, remained unintelligible until our later work had shown the ease with which bromine is replaced by hydrogen in these substances.

When at last the nature of this benzyl derivative was understood, it became one of our strong arguments in favor of the hexabromodiacetyl formula, which was established without question by the molecular weight determinations, the analyses of the other reduction products, and especially by the fact that the compound formed from it by the action of acetone was identical with tetrabromodiacetyl made from bromine and diacetyl in its melting point 94–95° (uncorr.), and in its very characteristic yellow coffin-shaped crystals. The heptabromomethyldiacetyl and its derivatives therefore must be struck from the list of known compounds.

So far as we can find, hexabromodiacetyl has been prepared only from tetrabromo-*o*-quinone as described in this paper. Some attempts of our own to prepare it with bromine and diacetyl led only to the known tetrabromodiacetyl in confirmation of the work of our predecessor,[1] and when we tried to introduce more bromine into this substance by exposing a mixture of it with bromine to the sunlight, no action was observed. Upon heating the mixture in a sealed tube an action took place, but the product was so tarry that we did not continue our experiments in this direction.

The most striking property of the hexabromodiacetyl is the ease, with which it forms the monomethylhemiacetal $CBr_3COC(OHOCH_3)CBr_3$ melting at 105° (uncorr.), or the corresponding ethyl compound melting at 96–97° (uncorr.) by standing in the cold with the alcohol.[2]

So far as we know, these are the first hemiacetals prepared from diketones with open chains, but such compounds have been obtained from ring diketones and the closely related para and orthoquinones.[3] This easy formation of hemiacetals from hexabromodiacetyl $CBr_3COCOCB_3$ seemed to us to deserve study, but we have had time to try only a few experiments, and therefore all the statements which follow are liable to revision after a fuller study of this subject. It seems probable that the

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[1] Keller, *Ber.*, 23, 35 (1890).

[2] *Am. Chem. J.*, 50, 367 (1913). The melting points in this earlier paper are somewhat lower than those given above, which is principally due to our discovery that petroleum ether is an almost perfect solvent for these compounds.

[3] Zincke, Arnst, *Ann.*, 267, 319, 331; Jackson, Grindley, *Am. Chem. J.*, 17, 579 (1895); Jackson, MacLaurin, *Ibid.*, 38, 127 (1907); Jackson, Flint, *Ibid.*, 39, 80 (1908).

diketone structure is more favorable to the formation of hemiacetals than the ketone, since we were unable to make one by the action of alcohol on pentabromoacetone; but in spite of this the diketones apparently stand at the bottom of the list of hemiacetal producing compounds, since it was necessary to have this structure reinforced by the 6 atoms of bromine, neither tetrabromodiacetyl, nor dibromodiacetyl, nor diacetyl itself showing any trace of the formation of a hemiacetal, when treated with alcohol. Aldehydes and quinones on the other hand need much less help from the presence of halogens, the monochloroaldehyde certainly forming a hemiacetal, and it is even possible that aldehyde itself does, although the evidence in this case is not convincing.[1] Tetraethoxy-*p*-quinone also forms an unstable hemiacetal, although in this case by the action of sodium alcoholate instead of alcohol, and both the para and orthoquinones give stable hemiacetals with much less halogen (2 to 3 atoms) than the diketone.

The hemiacetals derived from hexabromodiacetyl show a remarkable stability toward acids. In fact we have not succeeded in recovering the diacetyl from them, whereas chloral alcoholate is decomposed by strong sulfuric acid in the cold, and the hemiacetals of the paraquinones even by dilute hydrochloric acid at ordinary temperatures, while those of the orthoquinones, although more stable, yield to acids at higher temperatures. It is interesting that in these cases the greater stability belongs to substances with the carbonyls adjacent. In view of the easy formation of hydrates from substituted aldehydes it is strange that we have observed no sign of the formation of a hydrate from hexabromodiacetyl.

In all the hemiacetals isolated by us only one of the carbonyls of the hexabromodiacetyl was affected by the alcohol, but there are some indications that the action could extend to the other also, since, when the diketone stood for a long time with absolute methyl alcohol, a thick, red oil was obtained instead of the crystalline hemiacetal, and, when it was boiled with the alcohol, a less pure product resulted than in the cold. Both of these observations can be explained by the formation of a dihemiacetal, but more experiments are necessary before this explanation is accepted. The orthoquinones show a similar tendency to form monohemiacetals.

We consider these compounds hemiacetals, because we can find no other way in which the alcohol could be attached to the diketone; and this view is supported by the formation of an oxalic ester in addition to bromoform[2] when the ethyl compound was decomposed with water at 100°. Some of their properties however, are different from those we should have expected of hemiacetals. For instance, their stability toward acids,

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[1] Jacobsen, *Ber.*, **4**, 215 (1871); Renard, *Ibid.*, 8, 132 (1875).

[2] *Am. Chem. J.*, **50**, 368 (1913).

since they were not decomposed by boiling hydrobromic acid, or by dilute sulfuric acid boiling at 135°. At 150° the acid decomposed them, but no hexabromodiacetyl was recovered. Further acetic anhydride or acetyl chloride had no action on them in spite of the hydroxyl they contain. Although these properties are unexpected, they are not incompatible with the hemiacetal formula. These hemiacetals are somewhat more stable toward alkalies than the hexabromodiacetyl, but are decomposed by them with the formation of bromoform, and at least in the ethyl compound an oxalic ester. A greater stability is also shown by the fact that they are unaffected by hydriodic acid, which acts on the mother substance in a way to be described presently.

The hexabromodiacetylmonomethylhemiacetal was observed in 3 different sorts of crystals, when the solvent used was petroleum ether. (*a*) Long needles; (*b*) short broad square ended prisms, which may have been only a different habit of the first form; and (*c*) octahedra apparently of the tetragonal system, whereas the other two seemed to be orthorhombic. This last form also has a much more brilliant lustre than the others. All three melted at 105° (uncorr.), and could be converted into the first form by recrystallization. On the other hand the ethylhemiacetal was observed only in long narrow plates.

Benzyl alcohol acted on the hexabromodiacetyl in a more complex way than the fat alcohols, giving a compound containing only 5 atoms of bromine, for which we have worked out 2 constitutional formulas, either pentabromodiacetylmonobenzylhemiacetal $CHBr_2COC(OHOC_7H_7)CBr_3$ or benzyloxypentabromodiacetyl $C_7H_7OCBr_2COCOCBr_3$. We give the preference to the first of these formulas for the following reasons: the percentages of hydrogen found agree very well with this formula, but differ from that required by the second by a greater amount than is found in any other work by the two analysts who made them. The formation of a hemiacetal is characteristic of the behavior of the other alcohols with hexabromodiacetyl, whereas no other alkyloxy compounds have been observed. Hexabromodiacetyl undergoes the replacement of bromine by hydrogen also with acetone or hydriodic acid. The substance is more stable toward alkalies than the mother substance; this property is shown by other hemiacetals, whereas a substance with the second formula would probably be less stable. Alkalies give no bromoform with it.

Metanitrobenzyl alcohol did not combine with hexabromodiacetyl.

A few attempts to reduce the carbonyls in hexabromodiacetyl gave unsatisfactory results, but hydriodic acid converted it into tetrabromodiacetyl by replacing 2 atoms of bromine by hydrogen; and the same product was obtained more easily with acetone in the cold. If alcohol was mixed with the acetone, the product contained pentabromodiacetylmonoethylhemiacetal $CHBr_2COC(OHOC_2H_5)CBr_3$ melting at 115° (uncorr.); but acetone **mixed** with methyl alcohol gave no replacement of bromine by hydrogen, the only product being hexabromodiacetylmonomethylhemiacetal.

In forming the pentabromohemiacetals the replacement of bromine by hydrogen would be likely to take place in the CBr_3 next the unaltered carbonyl, if it happened after the formation of the hemiacetal (which is by no means established); and this view is supported by the observation that no bromoform could be detected, when the ethyl, or benzyl pentabromo compound was decomposed by an alkali, whereas the hexabromohemiacetals give bromoform under these conditions. We have therefore formulated these compounds accordingly.

When hexabromodiacetyl was treated with an aqueous solution of potassium iodide, iodine and carbonic dioxide were set free, and a new compound obtained, which melted with decomposition at 120–125°. We think that this substance is the triiodobromoacetone CI_3COCH_2Br, but cannot support this opinion by conclusive evidence. The discussion of this subject will be found in the Experimental Part.

The substance melting at 71–72° mentioned in the previous paper[1] as formed by the action of water on the hexabromodiacetyl, and also as a secondary product in its preparation has been recognized as pentabromoacetone. It was also obtained by the action of perhydrol, or constant boiling hydrobromic acid at 100° on the hexabromodiacetyl. We are unable to understand the mechanism of these reactions, but they are not without analogy, as pentabromoacetone is also formed by the action of hydrogen dioxide on tetrabromodiacetyl.[2]

Experimental.

Preparation of Hexabromodiacetyl,[3] $CBr_3COCOCBr_3$.—The process used by us differs in some important details from that described in the previous paper, and is therefore given in full. 200 g. of sodium hydroxide were dissolved in a litre of water, and after cooling to a few degrees above zero, 100 g. of tetrabromo-*o*-quinone were added in small portions at a time with constant shaking. If impure orthoquinone was used, the same product was obtained, but the yield was materially lowered. The green color, which appeared at first, gradually changed to brown, and at the same time enough gas was given off to cover the surface of the solution with foam. The mixture was allowed to stand in ice for 2–3 hours, and then at room temperatures for about 5 hours, after which it was poured into 400 cc. of strong hydrochloric acid (more than enough for neutralization) slowly and with constant cooling, so that the tem-

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[1] Jackson, Fiske, *Am. Chem. J.*, **50**, 366 (1913).

[2] Keller, Maas, *Centralb.*, 1898, I, 24.

[3] This substance was supposed by Fiske and one of us to be heptabromomethyldiacetyl (*Am. Chem. J.*, **50**, 360 (1913)). See the introduction to this paper.

perature of the mixture should never rise above luke warm. The yellowish brown flocculent precipitate of tetrabromopyrocatechin formed in this way was filtered off after settling for 5–10 minutes. To the filtrate were added 2 cc. of bromine, and the mixture shaken, until it was entirely absorbed. This treatment was repeated, till the presence of an excess of bromine was shown by the reddish color of the liquid, which required 23–25 cc., if the tetrabromo-*o*-quinone was pure, 13–18 cc., if it was crude. During the treatment with bromine the red liquid became at first milky, then began to give off carbon dioxide, and toward the end of the process a yellow precipitate appeared. In 5–10 minutes after the end of the treatment this precipitate had settled, when it was filtered out, and allowed to stand on a porous plate until thoroughly dry, which took about a day. An additional amount of decidedly impure product was obtained by allowing the filtrate to stand over night with 5 cc. of bromine. The dry precipitate was powdered, and extracted with successive portions of petroleum ether (boiling 30–50°), until the yellow substance was completely removed leaving a brown, tarry impurity. Upon distilling off the larger part of the petroleum ether, and cooling the residue, the hexabromodiacetyl crystallized out in a pure state, as shown by its melting point 100–101°[1] (uncorr.), which was not raised by recrystallization from petroleum ether. The yield varied from 21 to 24 g. from 100 g. of tetrabromo-*o*-quinone, but fell as low as 12 g., if crude material was used. The analyses of this substance will be found in the introduction.

Properties of Hexabromodiacetyl.—It crystallizes from petroleum ether in orange yellow plates shaped like arrowheads, and melts at 100–101° (uncorr.) instead of at 97–98° as given in the previous paper. This difference is probably due to the removal of the tarry impurity left after repeated extractions with petroleum ether. It is easily soluble in alcohol, methyl alcohol, ether, benzene, carbon tetrachloride, or glacial acetic acid; slightly soluble in petroleum ether, which is the best solvent for it; essentially insoluble in water. It is very stable toward acids, the three strong acids having no action on it in the cold, or on short warming to 100°. Fuming nitric acid when boiling dissolves it, but on cooling the substance crystallizes out to all appearance unaltered. Analyses showed however, that it had lost 1–2% of bromine. Boiling for several hours with strong nitric acid seems to decompose it completely. Boiling with sulfuric acid diluted with its own volume of water gives bromoform, but in such small amount that only a very slight decomposition is indicated. Water, hydric dioxide or constant boiling hydrobromic acid, while without effect on it in the cold, if heated with it to 100° in a sealed tube for 10 days, decomposes it, two of the products in each case being pentabromoacetone and bromoform. This behavior recalls the formation of penta-

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[1] In the previous paper it was given as 97–98°.

bromoacetone in a yield of 30–40% from tetrabromodiacetyl by the action of hydric dioxide. It is certainly strange that the substance should be distinctly less stable with water than with sulfuric acid. Hydriodic acid or acetone reduces it, as will be described later, and so will the action of potassium iodide.

In the hope of obtaining a dicyanhydrine similar to that yielded by tetrabromodiacetyl 15 g. of the hexabromodiacetyl mixed with 2–3 cc. of ether and 40 g. of a 40% aqueous solution of hydrocyanic acid were heated to 40° under a return condenser. The solid gradually went into solution, and after 5–10 hours the two layers of liquid formed at first were converted into a homogeneous mixture, which was allowed to stand over night, heated for a few more hours in the morning, and after cooling to 0° diluted with its own volume of water, and extracted with ether. The dried extract yielded only a yellow oil, which did not solidify on cooling, or standing for a month, and yielded only an oil on saponification with hydrochloric acid at 100°.

Alkaline reagents on the other hand decompose it easily. The hydroxide of sodium, potassium, or barium even in dilute solution converts it rapidly into bromoform and an oxalate; sodium carbonate acts in the same way but more slowly. A quantitative study of this reaction made by Fiske and one of us showed that two molecules of bromoform and one of oxalic acid were formed. Hot sodium methylate gave the same result; but in the cold a colorless product melting at about 80° was obtained, which has not been investigated. Boiling with an aqueous solution of sodium acetate also gave bromoform hydrobromic acid and oxalic acid; but when boiled with calcium carbonate and water, a sharp odor like that of a bromoketone was observed, and only tarry products were obtained. The same odor was produced by boiling with silver and water, but in this case oxalic acid and silver bromide were detected. A mixture of aqueous ammonia and alcohol gave in the cold oxamide; and aniline added to a benzene solution of the diketone gave oxanilid. *o*-Phenylenediamine gave somewhat impure *o*-phenyleneoxamide. Hydroxylamine hydrochloride had no apparent action; phenylhydrazine removed bromine from it; pyridine gave a black tar. No action was obtained with acetylchloride, or acetic anhydride, or benzoylchloride. Aqueous sulfurous acid did not act on it, even when standing several months with it. Zinc and acetic acid, or aluminum amalgam gave tars in preliminary experiments; but better results were obtained with hydriodic acid, as is described later. Bromine in the cold had no apparent effect upon it, and when heated with it in a sealed tube, tarry products were formed. The most interesting behavior of the diketone is that with alcohols, which is therefore described in detail.

Action of Hexabromodiacetyl with Alcohols. Hexabromodiacetylmonomethylhemiacetal, $CBr_3COC(OHOCH_3)CBr_3$.—This substance was prepared by allowing a solution of hexabromodiacetyl in methyl alcohol to stand for 4–5 days. A less pure product was obtained by the aid of heat. Absolute methyl alcohol should not be used in this preparation, as it forms an oily substance; in fact in an experiment, which stood for 2 weeks, very little hemiacetal was obtained, the chief product being an unmanageable thick, red oil. Even with ordinary methyl alcohol a little of this oil was formed, and therefore after the methyl alcohol had evaporated spontaneously, the residue was allowed to stand on a porous plate, after which it was recrystallized from petroleum ether, until it showed the melting point 105° (uncorr.). Analyses of this substance are given in the table in the introduction. 10 g. of diketone yielded 5 g. of the hemiacetal.

Properties of Hexabromodiacetylmonomethylhemiacetal. — Three sorts of crystals of this substance were obtained from petroleum ether, which differed so much in appearance that it certainly crystallizes in 3 different habits if not in 3 crystalline forms. On cooling, or rapid evaporation of the solution, most of the crystals are slender, long prisms, sometimes with a bluntly pointed end, sometimes with a square end; these turn opaque, when exposed to the air, but without loss of weight. The second form consists of short, square-ended prisms like slightly elongated cubes, usually bevelled on the edges, more rarely on the ends. These predominate when the evaporation is carried on slowly; but in most crystallizations both forms appear, and one is converted at least partially into the other by recrystallization. We do not feel certain that these are not different habits of the same crystalline form in spite of the great difference in their appearance. The third sort of crystal on the other hand seems distinctly to belong to a different system, for, while we should call the other two forms orthorhombic, or perhaps monoclinic, this third one seems to be tetragonal, since it consists of octahedra modified by many small planes, the two most conspicuous sets either truncating two opposite angles, or else the 4 edges of the octahedron the opposite angles then being unmodified. The vertical axis is but little longer than that of a regular octahedron, but in no case did we observe similar modifications on all the angles or edges. This form also has a much more brilliant lustre than the other two. We obtained it only once, and could not again find the conditions, under which it is formed. On recrystallization from methyl alcohol it is converted into the one first described. All three forms contain the same % of bromine.

The hemiacetal when crystallized from petroleum ether melts at 105° (uncorr.), but, if methyl alcohol is used, the melting point cannot be raised to this temperature, which explains the lower melting point (100–101°)

given in the earlier paper. This is obviously due to an action of the methyl alcohol upon it, which was also shown by the fact that such a solution although colorless at first turned yellow in a few minutes, but from this solution colorless crystals were obtained. As already stated, absolute methyl alcohol, if allowed to stand with it for some weeks, converts it into a red oil. The most obvious explanation of this action is that the dihemiacetal is formed, but this is rendered doubtful by the facts that the benzene solution also turns yellow on standing exposed to the air, and upon evaporating the benzene solution used in the molecular weight determination the residue was brownish. The crystals show a tendency to turn brown, when exposed to the air especially if moist. This apparent instability is surprising in view of the fact that it offers a strong resistance to the action of acids, strong nitric acid dissolving it apparently unchanged, while it was not decomposed by sulfuric acid diluted with its own volume of water, until it had been boiled with it some time. Then it formed an oil smelling like camphor. It is easily soluble in all the common organic solvents except petroleum ether, in which it is less soluble. This is the best solvent for it. It distils slightly with steam. It is unstable toward alkalies since alcoholic ammonia forms ammonium bromide; and aniline gives an oil. Hydroxylamine hydrochloride, acetic anhydride, or acetyl chloride does not act on it. A methyl alcohol solution boiled with finely divided silver gives an oil and a few white crystals melting near 70°.

Hexabromodiacetylmonoethylhemiacetal, $CBr_3COC(OHOC_2H_5)CBr_3$.—Ten grams of hexabromodiacetyl dissolved in 150 cc. of alcohol were allowed to stand at ordinary temperatures for 2–3 days, after which the alcohol was allowed to evaporate spontaneously. If the solution was heated, the product was less pure. The yellowish white crystals thus obtained, after standing on a porous plate, were crystallized from petroleum ether, until they showed the constant melting point 96–97°. The yield after one crystallization was 6 g. The analyses will be found in the table in the introduction.

Properties of Hexabromodiacetylmonoethylhemiacetal.—It crystallizes in narrow plates often 2–3 cm. long terminated by two planes at different angles to the sides, less commonly by one of these planes, so that there is either a blunt, or a very sharp end, according to which of the planes is present. It turns brown easily, when exposed to the air, especially if moist; after this change the percentage of bromine had fallen about 2%. It melts at 96–97° (uncorr.) instead of 93–94° as given earlier. It is easily soluble in alcohol, methyl alcohol, ether, acetone, or ethyl acetate; soluble in benzene, chloroform, tetrachloride of carbon, or glacial acetic acid; slightly soluble in petroleum ether, which is the best solvent for it; essentially insoluble in water. It distils with steam, although with difficulty.

When the monoethylhemiacetal was heated in a sealed tube with water to 100° for several days, the products were carbon dioxide, bromoform, hydrobromic acid, and probably monoethyloxalic ester, as the diethylester was obtained from it by distillation.[1]

As this substance could be prepared more easily than the methyl compound, it was studied in greater detail, and we tried especially to convert it back again into the hexabromodiacetyl but without success. Four experiments were tried with boiling dilute sulfuric acid, in which the water was allowed to evaporate, until the boiling point had risen from 110 to 135°, and at this temperature the boiling was continued for some time under a return condenser. The ethyl compound turned slightly yellow, but was recovered unchanged in every case. On heating to 150° for a few hours with strong sulfuric acid the substance was decomposed, forming a dirty yellow solution, but no hexabromodiacetyl could be detected. Boiling with constant boiling hydrobromic acid for 3 hours, or heating with it to 100° in a sealed tube produced no change. This marked stability toward acids is striking in view of the ease, with which it decomposes when moist, or when heated with water.

Sodium hydroxide decomposes the hexabromodiacetylmonoethylhemiacetal giving bromoform and a little oxalate, while barium hydroxide acts in a similar way, but only a trace of oxalate is formed. Sodium carbonate gives over 10% more bromoform than that required for one molecule, but only about half the calculated amount of oxalic acid. Sodium methylate also decomposes it, even when used in the proportion of only one molecule. In all these reactions with alkaline substances it was observed that the hemiacetal is distinctly more stable than the diketone. Ammonia, or aniline forms only tars, but also acts slowly. Hydroxylamine hydrochloride had no action on it.

Acetic anhydride, or acetyl chloride dissolves the hemiacetal, but no reaction takes place even after standing 4–7 days. If sodium acetate is used with the acetic anhydride, a yellow color appears, but the slight decomposition is probably due to the action of the salt. When the substance is heated to 120° over night with acetyl chloride, a sweet swelling oil is obtained, which deposits crystals of the unchanged monoethylhemiacetal, but the amount which reacts is so small that we could not study the product. Acetic anhydride when hot also gives an oily derivative. Zinc and acetic acid give small amounts of oil. When the hexabromodiketone is heated with alcohol, instead of reacting with it in the cold, tarry products are obtained with an odor like that of a bromoketone.

Pentabromoacetone.—In the preparation of hexabromodiacetyl the filtrate from it was mixed with 5 cc. of bromine, and allowed to stand

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[1] Anschütz, *Ber.*, 16, 2413 (1883).

over night, when a red oil was deposited, which changed to a sticky crystalline mass, if it was allowed to stand a few days in an open beaker, after the water had been separated. Most of the oil was then removed by a porous plate, and the residue crystallized by the slow evaporation of its solution in petroleum ether. The crystals were partly orange yellow hexabromodiacetyl, partly a white substance, which was separated mechanically, and after crystallization from petroleum ether melted constant at 73° (uncorr.). Although the melting point of pentabromoacetone is 76°, our analyses showed that our product is this substance.

Calc. for CBr_3COCBr_2H: C, 7.95; H, 0.22; Br, 88.31; M. W., 453. Found: C, 8.50; H, 0.46; Br, 88.30; M. W., 388, 413, 417.

The same compound was formed by heating hexabromodiacetyl for 10 days at 100° in a sealed tube with water, perhydrol, or constant boiling hydrobromic acid; bromoform was also formed in each case.

When hexabromodiacetyl stood for several days with amyl alcohol, the product, after being freed from unaltered alcohol by a blast of air, was a yellow oil, which to our great surprise contained an amount of bromine only 1% too high for that required by the monoamylhemiacetal.

Pentabromodiacetylmonobenzylhemiacetal, $CBr_2HCOC(OHOC_7H_7)$-CBr_3.—Five grams of hexabromodiacetyl were heated on the water bath in a 25 cc. flask with 5–6 g. of benzyl alcohol for 10 hours. At the end of this time the residue was distilled with steam, which carried over the excess of benzyl alcohol and the benzyl bromide formed. The yellowish oil, which had not distilled with the steam, was allowed to stand until it had crystallized, and then after being freed from oil with a porous plate it was crystallized from naphtha boiling between 70° and 100°, until it showed the constant melting point 109–110° (uncorr.). The yield varied from 2 to 2.5 g. The analyses given in the introduction show that the substance is the pentabromodiacetylmonobenzylhemiacetal. The hydrobromic acid formed in this reduction was detected in the water, with which the product was distilled, and had also converted some of the benzyl alcohol into benzylbromide as was shown by its violent action on the eyes.

Properties of Pentabromodiacetylmonobenzylhemiacetal.—It crystallizes from ligroin in large, thick, rhombic prisms, which melt at 109–110° (uncorr.). It is easily soluble in alcohol, methyl alcohol, ether, benzene, or glacial acetic acid; less soluble in ligroin, which is the best solvent for it; essentially insoluble in petroleum ether, or water. Strong sulfuric acid, nitric acid, hydrochloric acid, or hydrobromic acid has no apparent effect on it. It is more stable toward alkalies than the hemiacetals of hexabromodiacetyl, as barium hydroxide did not attack it at all even on standing with it for 2 days, and sodium hydroxide did not decompose it completely, until it had stood with it several days. The yellow oil thus obtained contained no bromoform. Acetyl chloride, or acetic anhydride has no action on it, in fact it crystallizes very well from the anhydride, the crystals showing the melting point 109–110°, and containing 67.93% of bromine (calc. for the hemiacetal 67.92).

Metanitrobenzyl alcohol when heated on the water bath with hexabromodiacetyl was converted into *m*-nitrobenzyl ether, and this was the only product found, the diacetyl having apparently decomposed completely. Phenol formed with hexabromodiacetyl an unpromising black mass.

Attempts to make hemiacetals by contact with alcohols yielded no results with tetrabromodiacetyl, dibromodiacetyl, diacetyl, benzil, or pentabromoacetone.

Reduction of Hexabromodiacetyl.—Reduction experiments with zinc and acetic acid, or sulfuric acid yielded only a few drops of oil; but acetone, or hydriodic acid gave a better result. Five grams of hexabromodiacetyl were dissolved in acetone, and allowed to stand 4–5 hours[1] at ordinary temperatures, after which the solution was allowed to evaporate spontaneously under the hood, because of the bromoacetone. On standing over night a hard mass was obtained, which after removing the last of the bromoacetone by a porous plate was crystallized from petroleum ether, until it showed the constant melting point 94–95° (uncorr.). This suggested that it was tetrabromodiacetyl, which melts at this temperature. Accordingly a specimen of this compound was prepared from diacetyl, when it was found to coincide with our product in every respect, the yellow crystals from carbon disulfide being especially characteristic, as they consisted of rhombic plates with the acute angles truncated, and in every case one of these truncating planes was nearer the obtuse angles than the other giving the crystals the shape of a coffin. For greater certainty our product was analyzed.

Calc. for $CHBr_2COCOCHBr_2$: C, 11.94; H, 0.50; Br, 79.60. Found: C, 12.07; H, 0.85; Br, 79.68, 79.58.

Hydriodic acid produced the same substance, when 1 g. of hexabromodiacetyl previously moistened with water was shaken with 2 cc. of the constant boiling acid. After filtering out the iodine the filtrate was extracted with ether, or allowed to evaporate. The product was recognized by its melting point 94–95° (uncorr.) as tetrabromodiacetyl, which is moderately soluble in water.

Pentabromodiacetylmonoethylhemiacetal, $CBr_2HCOC(OHOC_2H_5)CBr_3$.—Ten grams of hexabromodiacetyl dissolved in 150 cc. of alcohol and 15 cc. of acetone were allowed to stand 5–8 weeks at ordinary temperatures. The product, after the solvents had evaporated spontaneously, consisted of two substances, the hexabromodiacetylmonoethylhemiacetal, and another, which was distinctly more soluble in alcohol, and therefore

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[1] Longer standing yielded the same product.

was washed away from the hexabrom compound with this solvent. The separation thus roughly effected was completed by crystallization from petroleum ether, in which the hexabrom compound is less soluble. In this way the constant melting point 115° (uncorr.) was at last obtained. The analyses given in the introduction show this is the *pentabromodiacetylmonoethylhemiacetal.*

Properties.—It crystallizes from petroleum ether in short, broad prisms terminated by a second prism at right angles to the first, so that they look like somewhat lengthened octahedra. They are modified by many small planes. It melts at 115° (uncorr.); and is soluble in alcohol, methyl alcohol, benzene, tetrachloride of carbon, or glacial acetic acid; insoluble in water. Sodium hydroxide did not set free bromoform from it.

The following experiments to obtain the corresponding methyl compound gave negative results,—hexabromodiacetyl with methyl alcohol and acetone, its monomethylhemiacetal with acetone, or with methyl alcohol and acetone. The only substance isolated in each case was hexabromodiacetylmonomethylhemiacetal.

Action of Potassium Iodide on Hexabromodiacetyl.—To a solution of 3 g. of potassium iodide in 25 cc. of water was added 1 g. of powdered hexabromodiacetyl. A brown color soon appeared, which gradually grew darker, and was accompanied by the evolution of carbonic dioxide in large quantity. After 2 days a crystalline precipitate had formed, which was filtered out, washed with a solution of potassium iodide to remove the free iodine, and allowed to stand on a porous plate for 10–12 hours, at the end of which time the iodine had disappeared to judge from the color. It was not easy to find a good solvent for this substance, as most of the common ones set free iodine from it, but at last it was found that tetrachloride of carbon gave good crystals without a colored mother liquor, and accordingly it was crystallized 5 times from that, when it decomposed between 122 and 125°; but this point varied so much with the conditions of the heating that it is of little value as a criterion of purity. We therefore analyzed specimens from the first, second, third and fourth crystallizations, and found that the impurities had been removed by the first, as the results from the last 3 (given below) agreed with each other.

Subs. 0.1468, 0.2129, 0.1366, 0.1845, 0.2439, $AgBr.3AgI$ 0.2568, 0.3730, 0.2392, CO_2 0.0519, 0.0679, H_2O 0.0122, 0.0133. Found: BrI_3, 90.28, 90.44, 90.40; C, 7.67, 7.59; H, 0.78, 0.61.

The formula we assign to this substance is $C_3H_2BrI_3O$ which requires BrI_3 89.52, C 6.99, H 0.39, molecular weight 515 (found 475, 485, 502). These percentages do not agree very well with those found, but this is accounted for by the fact that the only solvent which did not decompose our substance was tetrachloride of carbon, and according to our experience substances crystallized from this usually give poor results on analysis.

If this empirical formula is correct, the substance is probably triiodobromoacetone, and we have adopted this structure for it provisionally.

Properties of Triiodobromoacetone?—It crystallizes from tetrachloride of carbon in slender, lemon-yellow needles, which turn brown in the light. It melts with decomposition at 122–125°, but this point is decidedly indefinite. It is soluble in alcohol, methyl alcohol, benzene, chloroform, or tetrachloride of carbon; essentially insoluble in petroleum ether. All of these solvents decompose it somewhat with liberation of iodine, but this action is least with tetrachloride of carbon, which is therefore the best solvent for it. Fuming nitric in the cold or strong nitric acid when heated decomposes it, setting free iodine. Nitric acid diluted with acetic acid had no action in the cold, but on warming iodine was set free. Ammonium hydroxide gave a smell like iodoform, and ammonium iodide was found in the liquid. Sodium hydroxide also gave iodoform to judge by the smell. Hydric dioxide did not act on it.

Hexabromodiacetylmonoethylhemiacetal was not affected by potassium iodide solution even at 100°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

NORMAL NONANE.

BY LATHAM CLARKE AND ROGER ADAMS.

Received August 16, 1915.

Normal nonane was first synthetically produced by Krafft,[1] by reduction of pelargonic acid, $C_9H_{18}O_2$, with hydriodic acid and phosphorus in a sealed tube heated to 240°. The boiling point at 760 mm. is given by Krafft as 149.5° and the specific gravity, compared to water at 4°, is as follows: 0°, 0.7330; 13.5°, 0.7228; 15°, 0.7217; 20°, 0.7177; 99.1°, 0.6541.

We found the boiling point as 150.4–150.6° at 759 mm. The specific gravity at 15°, compared to water at 15°, is 0.7219. The index of refraction, $n_D^{25°} = 1.4025$.

The starting point in the preparation of normal nonane was castor oil. By distillation this yielded oenanthol (normal heptyl aldehyde), which, after purification by means of the bisulfite compound, was treated with ethyl magnesium bromide giving, after the usual decomposition of the organo-magnesium derivative, ethyl hexyl carbinol, or 3-nonanol. This carbinol was converted into the corresponding carbinol iodide by treatment with iodine and red phosphorus, and the resulting 3-iodononane was boiled with alcoholic potash, which gave nonylene. This last yielded normal nonane on reduction.

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[1] *Ber.*, 15, 1692 (1882).