

acid mixture had to be cooled. After the action had subsided the mixture was warmed on the water bath for a few minutes. The chloropicrin was recovered as usual after steam distillation.

**Methyl Alcohol.**—Methyl alcohol remains undecomposed by aqua regia even on warming on the water bath and hence no chloropicrin is produced. After a very prolonged action only a slight smell of chloropicrin could be noticed.

**Formic and Acetic Acids.**—These acids are quite stable and remain undecomposed even on warming. Consequently no chloropicrin is formed in these cases.

A host of other substances has been found to give chloropicrin as the ultimate decomposition product, and it appears that the production of chloropicrin might be quite general. Investigations to establish this as well as a general study of the action of aqua regia and also the action of nitric acid in conjunction with bromine and iodine on organic bodies are being continued.

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## CONTRIBUTIONS TO THE KNOWLEDGE OF HALOGENATION. VII.<sup>1</sup> SUBSTITUTED NITROGEN CHLORIDES. THE ACTION OF CHLORINE ON CARBAMIC ESTERS AND BIURETS AND THE PREPARATION OF CHLOROCAR- BAMIC ESTERS AND CHLOROBIURETS.

BY RASIK LAL DATTA AND SATYARANJAN DAS GUPTA.

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The action of chlorine on ethyl carbamic ester has been studied by us<sup>2</sup> with the isolation of monochlorocarbamic ester. Schmidt<sup>3</sup> obtained a condensation product of urethane with dichloroacetaldehyde, *viz.*, dichloro-ethylidene urethane by the action of the same reagent on the ester at a high temperature.

It has been found that the chloroderivatives of other esters of the series can be prepared by working with aqueous solutions of the urethanes in the cold. These have been specially isolated since they might serve as useful synthetic reagents on account of their greater stability than similarly substituted carbamide derivatives. It has been noted under monochlorocarbamic ester, that it readily serves for the chlorination of amines and amides which hitherto had to be chlorinated by means of alkaline

<sup>1</sup> Previous communications on the subject; see Datta, *J. Chem. Soc.*, 101, 166 (1912); Datta and Ghosh, *THIS JOURNAL*, 35, 1044 (1913); Datta and Gupta, *Ibid.*, 36, 386 (1914); Datta and Fernandes, *Ibid.*, 36, 1007 (1914); *Ibid.*, 36, 1011 (1914); Datta, *Ibid.*, 36, 1011 (1914).

<sup>2</sup> Datta and Gupta, *THIS JOURNAL*, 36, 386 (1914).

<sup>3</sup> Schmidt, *J. prakt. Chem.*, [2] 24, 120 (1881).

hypochlorites. Besides, it has also been found that the monochloro-carbamic esters hydrolyze, giving rise to interesting condensation products. These compounds have been found to be extremely active, the chlorine in them being very loosely combined and they react vigorously with sodium. In fact these compounds promise to be of signal service in as mild chlorinating synthetic agents in the laboratory. The chloro-derivatives themselves are interesting since they represent a new class of substituted nitrogen chlorides which it has been our object to isolate. Besides the chloroderivatives of carbamic esters, the chloroderivatives of biuret and substituted biurets have been prepared.

It is very peculiar that no chloroderivative of the first ester of the series, *viz.*, methylcarbamic ester, could be prepared. It is, however, in keeping with the general notion that the first member of a homologous series behaves anomalously. The monochloroderivative of ethyl carbamic ester could be prepared by passing chlorine into a cold aqueous solution of the ester, as has been already described in a previous communication. In the case of ethylcarbamic ester, the monochloroderivative is the only product, however long the chlorination process is continued. But its next homolog behaves quite differently. Both monochloro- and dichloro-derivatives of propyl urethane could be obtained, although the latter could not be obtained pure, even when using chlorine in excess. The monochloroderivative could readily be prepared by passing a calculated quantity of chlorine into the aqueous solution of the urethane. Isobutyl carbamic ester can give rise to pure monochloroderivative although there is evidence of the formation of dichloroderivative, as is shown by the fact that the chlorine content approaches that of the dichloroderivative when chlorine is used in excess. In the case of the chlorination of isoamyl urethane, the monochloroderivative could not be prepared as an intermediate product, the dichloroderivative being formed at once.

Carbamic esters in which one or more amidic hydrogens are substituted, do not form the chloroderivatives at all. For instance, it has been found that chlorine has no action on chloral urethane. The action of chlorine on phenyl urethane is very peculiar, giving rise not to chloroderivatives, but to a complete condensation product. This might be accounted for by the fact that the phenyl radical, unlike the aliphatic radicals, easily takes part in condensation reactions. The action of chlorine on ethylidene ethyl carbamic ester is quite interesting. This breaks up during the chlorination process and dichloroethylcarbamic ester is the result, although the latter could not be prepared from ethyl carbamic ester itself under any conditions.

These compounds dissolve in almost all common organic solvents and are generally liquids of a pale yellow color. The boiling point, density and refractive index show a general regularity according to their increasing

molecular weights. The densities and refractive indices of the monochloroderivatives decrease while the boiling points increase with their increasing molecular weight.

The dichloroderivatives also show a similar behavior. On heating the liquids above their boiling points it was found that each had a temperature at which it decomposed with the separation of a solid product.

When these compounds are applied to the skin, a very painful sensation is produced and blisters are often formed which take considerable time to heal.

In the formation of these chloroderivatives substitution takes place with formation of hydrochloric acid, which remains dissolved in the mother liquor. As in other substituted nitrogen chlorides, the chlorine liberates iodine quantitatively from potassium iodide and this fact has been taken advantage of in analyzing these compounds.

#### **Action of Chlorine on Methyl Carbamic Ester.**

The action of chlorine on methyl urethane was studied under various conditions but in no case was it possible to isolate its corresponding chloroderivative. It appears that it is not capable of forming a chloroderivative.

Chlorine was first passed through a dilute solution of the ester, but even after passing it for a considerable time no sign of separation of the desired product was evident, although the peculiar smell belonging to this class of chloro compounds was perceived. It was thought that the great solubility of the chloroester might prevent its separation. To overcome this a saturated solution of methyl urethane was subjected to the prolonged action of chlorine, but in this case also, the solution only gave the peculiar smell due to chloroderivatives.

In order to determine whether the great solubility of the chloroderivative, together with the presence of the hydrochloric acid formed in the solution as a result of the reaction, prevented the reaction from proceeding beyond a limited extent the action of chlorine was next tried on the finely powdered urethane with only a few drops of water. The mass liquefied in a few minutes while the chlorine was passed into it. On examining the product, however, it was found that only a very small quantity of the substance was transformed into the chloroderivative. This causes the whole substance to liquefy and prevents further chlorination in accordance with the reason put forward above.

Finally it was decided to try the action of dry chlorine on the dry substance but no reaction took place. Nor was chlorination obtained when chlorine was passed into molten methyl urethane, the resulting product being unchanged methyl urethane.

**Action of Chlorine on Propyl Urethane, Monochloropropylurethane,**  
 $\text{NHCl}-\text{CO}-\text{OC}_3\text{H}_7$ .—The action of chlorine on propyl urethane results in formation of both monochloro- and dichloroderivatives, according as the

chlorination is stopped at an intermediate stage or carried to completion. An attempt was first made to prepare monochlorourethane by passing a rapid current of chlorine through a saturated aqueous solution of propyl urethane. Within a few minutes, a liquid began to separate. This was separated, dried and the halogen estimated. A much higher value than is required for the monochloroderivative was obtained. That the high percentage of chlorine was not due to chlorine dissolved in the liquid was shown by washing with water and dilute alkali which did not change the chlorine content. Hence, it was quite evident that the higher percentage of chlorine was due to the formation of some dichloroderivative. Since the liquid boils with decomposition, a separation could not be effected by distillation. Finally, the monochloroderivative was prepared by passing a calculated amount of chlorine into an aqueous solution of the substance, when the desired product separated as a pale yellow oil in the pure state.

0.2682 g. required 20.0 cc. 0.1 *N* thiosulfate; Cl as NaCl = 26.51.

0.2143 g. gave 0.2272 g. AgCl by Carius's method; Cl = 26.23.

0.1564 g. gave 0.1976 g. CO<sub>2</sub> and 0.0774 g. H<sub>2</sub>O; C = 34.46; H = 5.49.

0.0974 g. gave 8.6 cc. N<sub>2</sub> at 30° and 760 mm.; N = 10.23.

Calc. for C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>NCl, C = 34.69; H = 5.83; N = 9.78; Cl = 25.82.

The substance is a pale yellow oil having, at 30°, a specific gravity of 1.269 and a refractive index of 1.45377. It is soluble in ether, methyl alcohol, ethyl alcohol, acetone, chloroform, carbon tetrachloride and benzene. With some of these solvents it is miscible in all proportions. Its action on the skin is a little less energetic than its lower homolog ethylchlorocarbamic ester. It takes a longer time for the first sensation of pain and the appearance of the blister on the skin. Its action on amines and acid amides is quite similar to that of its lower homolog. By its action both monochloro- and dichlorobenzylamines could be prepared from benzylamine, according as the one or the other be employed in excess. Benzamide was similarly chlorinated by means of it, with the production of the monochloroderivative.

**Dichloropropylurethane, NCl<sub>2</sub>—CO—OC<sub>3</sub>H<sub>7</sub>.**—For the preparation of the dichloroderivative an excess of chlorine was passed through a well-cooled, saturated solution of the ester when it was obtained as a pale yellow mobile liquid. The product was washed and dried as usual.

0.2676 g. required 28.6 cc. 0.1 *N* thiosulfate; Cl as : NCl = 37.93; calc. for C<sub>2</sub>H<sub>7</sub>NO<sub>2</sub>Cl<sub>2</sub>, Cl = 41.28.

As appears from the analysis above, the pure dichloroderivative could not be prepared. It is quite possible that during its formation in the presence of water, some of the monochloroderivative remains unchanged. Its properties are quite similar to the monochlorourethane as regards its solubility, action on amines and acid amides and action on the skin.

**Monochloroisobutylurethane**,  $\text{NHCl}-\text{CO}-\text{OC}_4\text{H}_9$ .—Like propylurethane, butyl urethane undergoes chlorination with the formation of both monochloro- and dichloroderivatives although the latter could not be prepared even in a state approaching purity. It is obtained as a mixture with the monochloroderivative. The monochloroderivative could be prepared similarly to monochloropropylurethane by passing a calculated amount of chlorine through a well-cooled aqueous solution of the urethane, when it separated as a pale yellow, mobile liquid having the characteristic odor of the chlorourethanes. It was washed and dried as usual.

0.1751 g. required 11.3 cc. 0.1 *N* thiosulfate; Cl as : NCl = 22.84. 0.2010 g. gave 0.1876 g. AgCl by Carius's method; Cl = 23.09. Calc. for  $\text{NHCICO}-\text{OC}_4\text{H}_9$ , Cl = 23.44.

The substance is a pale yellow, mobile liquid having a specific gravity of 1.156 and a refractive index of 1.44615 at 30°. The compound begins to boil with decomposition at 140° leaving off a white solid. At the same time white vapors are given out which condense on the upper and cooler parts of the tube. Its action on the skin is a little less energetic than its lower homolog and its behavior towards amines and acid amides is the same as that of its lower homologs, giving rise to chloroderivatives.

When a large excess of chlorine is used and the current is continued even after the separation of oil, there is a tendency for the formation of the dichloroderivative although it could not be obtained in a state of purity. It is obtained as a mixture of monochloro- and dichloroderivatives. In one experiment the percentage of chlorine went as high as 30.5%, the values calculated for monochloroderivative being 23.4 and that for the dichloroderivative 38.17%. As no method could be found to effect a separation the dichloroderivative could not be prepared in a pure state.

**Dichloroisoamylurethane**,  $\text{NCl}_2-\text{CO}-\text{OC}_5\text{H}_{11}$ .—The action of chlorine on isoamylcarbamic ester gives rise at once to the dichloroderivative and the monochloro product could not be obtained at all, even by stopping the chlorination process at an intermediate stage. For the preparation of the dichloroderivative a current of chlorine is passed into a quantity of powdered isoamylurethane suspended in water. The mother liquor, which at the beginning appears like a white emulsion, becomes quite clear after saturation with chlorine and the required product separates as a yellow oil. The oil was washed and dried as usual.

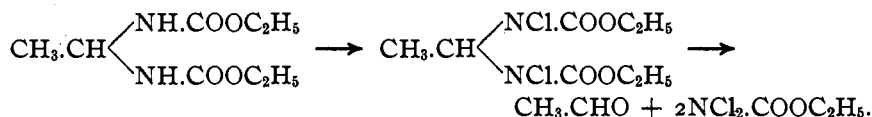
0.0957 g. required 9.45 cc. 0.1 *N* thiosulfate; Cl as : NCl = 35.01. Calc. for  $\text{C}_5\text{H}_{11}\text{O}_2\text{NCl}_2$ , Cl = 35.5.

The substance has a specific gravity of 1.156 and a refractive index of 1.45146 at 30°. It is soluble in ordinary solvents. Its action on the skin and on amines and acid amides is quite the same as that of its lower homologs. The compound begins to boil at 124°. At 145° dense white vapors arise from the surface of the liquid and the reaction is so vigorous

that it is accompanied by a sudden flash of light; at the same time a crystalline brown solid separates from the liquid.

**Action of Chlorine on a Ethylideneurethane, Dichlorocarbamic Ester,**  $\text{N}-\text{Cl}_2.\text{COOC}_2\text{H}_5$ .—The action of chlorine on ethylideneurethane is somewhat peculiar. It is a condensation product of acetaldehyde and ethyl urethane and it does not admit of chlorination before the rupture of the substance, and the rupture takes place with the formation of dichlorocarbamic ester, which could not be prepared by the direct action of chlorine on the ester as has been noted before.<sup>1</sup> Even by this method, the dichloroderivatives could not be prepared in a pure state, being contaminated with a little monochloroderivative. The action which takes place may be explained thus: One atom of hydrogen directly united with nitrogen is

chlorinated first to form at  $\text{CH}_3.\text{CH}$   $\begin{matrix} \text{NCl}.\text{COOC}_2\text{H}_5 \\ \text{NCl}.\text{COOC}_2\text{H}_5 \end{matrix}$  but on further action of chlorine the compound breaks up into  $\text{CH}_3.\text{CHO}$  and  $\text{NCl}_2.\text{COOC}_2\text{H}_5$  thus:



For the preparation of the compound, ethylideneurethane was first powdered and suspended in water and then a rapid current of chlorine was passed through it. The solid gradually begins to change into oily globules which become more and more mobile and the whole of it finally changing into a mobile yellow oil when the action is complete. The liquid was separated from the mother liquor, washed and then dried. The yield amounted to about 60% of the theory.

0.1721 g. required 21 cc. 0.1 *N* thiosulfate; Cl as :  $\text{NCl} = 4.332$ . Calc. for  $\text{NCl}_2-\text{COOC}_2\text{H}_5$ , Cl = 44.93.

The low percentage of chlorine in the product may be accounted for by the presence of monochloroderivative as impurity, from which it could not be separated.

It is a pale yellow, mobile liquid having at 30° a specific gravity of 1.304 and a refractive index of 1.45397. It has a smell similar to the ethylmonochlorocarbamic ester and affects the skin like the monochlorocarbamic ester. Its action on amines and acid amides is the same as has been found with the other members of the series, this being the most active among them.

**Action of Chlorine on Chloralurethane.**—The action of chlorine on chloralurethane does not give rise to any chloroderivative. It appears that urethanes in which an amido group is substituted do not give chloro-

<sup>1</sup> *Loc. cit.*

derivatives unless they are decomposed into the original esters. In the case of ethylideneurethane it has been found that it decomposes into the original ester, the dichloroderivative of which is the result of the action of chlorine. But the stability of chlorourethane is considerable, owing to the electronegative character of the three chlorine atoms, and hence the compound remains unchanged on subjecting it to the action of chlorine under varying conditions.

**Action of Chlorine on Phenylurethane.**—The result of the action of chlorine on phenylurethane is quite interesting. Instead of giving rise to the usual chloroderivatives, a complex condensation product results. The first action might, no doubt, give rise to the usual chloroderivatives but the great reactivity of phenyl radical for substitution reactions might be the cause of the production of the condensation product.

A rather slow current of chlorine was passed through a quantity of phenylurethane suspended in water. At first a white emulsion came down which soon changed into a dirty gray, and then green, oily substance which afterwards turned to a pasty, brownish, solid mass. This was washed thoroughly with water and left to dry in a vacuum desiccator. The substance was first recrystallized from acetone and then again from ether. When crystals first form from an ethereal solution they appear perfectly white but after some time, and on keeping in a desiccator, they gradually turn to a very pale yellow color. On partially washing these crystals with successive small quantities of ether, white flakes of crystals remain behind. These crystals, on dissolving in alcohol and allowing to recrystallize undisturbed, give beautiful white needles. The substance had a sharp melting point of  $83^{\circ}$ . It is soluble in acetone, ether and alcohol. Its constitution could not be determined at present.

0.1321 g. gave 0.2102 g.  $\text{CO}_2$  and 0.0520  $\text{H}_2\text{O}$ , C = 43.40; H = 4.00. 0.1093 g. gave 7.8 cc.  $\text{N}_2$  at  $30^{\circ}$  and 760 mm., N = 8.10. 0.1426 g. gave 0.0816 g.  $\text{AgCl}$ , Cl = 14.16. Calc. for  $\text{C}_{18}\text{H}_{20}\text{N}_3\text{Cl}_2\text{O}_9$ , C = 43.72; H = 4.06; N = 8.50; Cl = 14.37.

**The Hydrolytic Product of Monochlorourethane.**—It has been shown previously that monochlorourethane undergoes hydrolysis when kept in contact with water and alkalies for a time extending over several days in presence of air. The compound is completely decomposed and a white crystalline substance is formed below the water. The substance was recrystallized from alcohol and had a sharp melting point of  $147^{\circ}$ . Many preparations were undertaken with the same results. The compound corresponds to the formula  $\text{C}_7\text{H}_{15}\text{N}_3\text{O}_4\text{Cl}$ .

0.0940 g. gave 0.1188  $\text{CO}_2$  and 0.0528  $\text{H}_2\text{O}$ , C = 34.47; H = 6.18. 0.1158 g. gave 17.00 cc.  $\text{N}_2$  at  $28.5^{\circ}$  and 763 mm., N = 17.20. 0.0583 g. gave 0.0344  $\text{AgCl}$ , Cl = 14.50. Calc. for  $\text{C}_7\text{H}_{15}\text{N}_3\text{O}_4\text{Cl}$ , C = 34.92; H = 6.23; N = 17.46; Cl = 14.77.

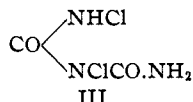
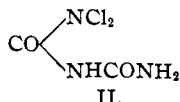
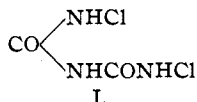
Its constitutional formula could not be assigned at present and further work is necessary to elucidate its constitution.

The hydrolytic products of the other chlorocarbamic esters are being studied and attempts are being made to apply them as synthetic agents.

### The Action of Chlorine on Biuret and Substituted Biurets.

Having been successful in isolating the various chloroderivatives of the different carbamic esters, which are in fact substituted nitrogen chlorides, it was thought possible to substitute by chlorine the hydrogen atoms united to nitrogen in more complicated derivatives derived from carbamide in which the amido groups of urea remain intact, *viz.*, biuret and substituted biurets. From biurets, dichlorobiuret has been obtained, and acetylbiuret gave rise to dichloroacetylbiuret. These are important on account of the fact that they represent a new class of substituted nitrogen chlorides which have hitherto not been prepared.

**Dichlorobiuret,  $\text{NHCl}-\text{CO}-\text{NHCONHCl}$ .**—The action of chlorine on biuret gives rise to a dichloroderivative and there are three possible formulas for the same, *viz.*,



But on careful consideration and study of the other substituted nitrogen chlorides, it can be safely asserted that Formula I is the only possible one. The second formula can be rejected on the ground that both atoms of hydrogen of one of the  $\text{NH}_2$  groups cannot be replaced when another symmetrically situated  $\text{NH}_2$  group remains unacted upon. Formula III can also be rejected, owing to the improbability of substitution by chlorine in an imido group in preference to that in an amido group.

A few grams of biuret were taken in a flask with a quantity of water insufficient to dissolve the whole at the ordinary temperature. The water was next warmed to  $60-70^\circ$  until all the biuret went into solution. When the solution had cooled somewhat, a rapid current of chlorine was passed through it when, within a very short time, a white precipitate began to form. This increased in quantity as the current of chlorine was continued. When it was found that the amount of precipitate no longer increased, the current of chlorine was stopped and the crystals obtained were filtered with suction and washed thoroughly with water. The substance thus obtained consisted of a crystalline white powder. It was then dissolved in alcohol and crystallized therefrom. The substance melted with decomposition at  $160^\circ$  with a sharp and sudden crackling sound.

0.1673 g. gave 0.8293 g.  $\text{CO}_2$  and 0.0328  $\text{H}_2\text{O}$ ; C = 13.52; H = 1.94. 0.0836 g. gave 17.8 cc.  $\text{N}_2$  at  $25^\circ$  C. and 764 mm., N = 24.69. 0.1813 g. gave 0.3007 g.  $\text{AgCl}$ , Cl = 41.03. Calc. for  $\text{C}_2\text{H}_3\text{O}_2\text{N}_3\text{Cl}_2$ , C = 13.59; H = 1.74; N = 24.42; Cl = 41.28.

This substance, like the other substituted nitrogen chlorides, liberates



iodine from potassium iodide. Hence a volumetric estimation was undertaken in order to determine whether it agreed with the volumetric estimation given above. However, a certain anomaly was noticed which calls for a special explanation. The analysis was carried out by adding a weighed quantity of the biuret derivative to a solution of potassium iodide and then titrating the liberated iodine with sodium thiosulfate. The percentage of chlorine as the mean of several analyses was found to be 51.35%, whereas that obtained by gravimetric method was only 41.03. The chlorine calculated for trichlorobiuret is 51.55. The gravimetric estimation gives as a rule the whole of the chlorine of a substance if carried out in sealed tubes by the Carius method. Hence the excess of chlorine found by the volumetric method is certainly due to some decomposition reaction of dichlorobiuret itself which liberates an equivalent quantity of iodine from potassium iodide.<sup>1</sup>

The action which takes place is one of substitution like the carbamides and carbamic esters, resulting in the liberation of hydrochloric acid which was found in the filtrate from the precipitated dichlorobiuret. The reaction is quantitative, unlike carbamide, since biuret is neutral and does not combine with hydrochloric acid, which therefore does not interfere with the chlorination.

The compound is quite stable, unlike the other substituted nitrogen chlorides which have a great tendency to decompose. A sample of the product was analyzed after being kept for nearly a month when all its chlorine was found intact although the substance could not be kept indefinitely. The compound was vigorously acted upon by a fairly strong solution of caustic potash but it dissolves to a yellow solution in a dilute solution of the same. It is fairly soluble in ether and insoluble in water and benzene.

**Dichloroacetylbiuret**,  $\text{NHCO.CH}_3\text{—CO—NHCONCl}_2$ . — Monoacetylbiuret was prepared according to the method of Schiff.<sup>2</sup> The monoacetylbiuret is dissolved in a small quantity of water by heating on the water bath to make a saturated solution. After cooling the solution to some extent, a rapid current of chlorine was passed into it when, within a few minutes, crystals began to appear. After passing chlorine for some time longer the solid was filtered off and washed with water in which it seemed to be slightly soluble. It is purified by crystallization from alcohol. The pure product melts with decomposition at  $170^\circ$  with a sharp crackling sound similar to that given by dichlorobiuret.

<sup>1</sup> The author has apparently overlooked the fact that compounds of the type of nitrogen trichloride liberate two atoms of iodine for each atom of chlorine present. See Hentschel, *Ber.*, 30, 1434. This is evidently because the chlorine is *positive* in these compounds. Noyes and Lyon, *THIS JOURNAL*, 23, 462 (1901); Noyes, *Ibid.*, 35, 767 (1913).—EDITOR.

<sup>2</sup> *Ann.*, 291, 377 (1896).

0.1380 g. required 13 cc. 0.1 *N* thiosulfate; Cl as : NCl = 33.31. 0.0933 g. gave 12.2 cc. N<sub>2</sub> at 29.8° and 763 mm., N = 19.80. 0.1701 g. gave 0.1387 g. CO<sub>2</sub> and 0.0379 g. H<sub>2</sub>O, C = 22.24; H = 2.47. Calc. for C<sub>4</sub>H<sub>5</sub>O<sub>3</sub>N<sub>3</sub>Cl<sub>2</sub>, C = 22.43; H = 2.34; N = 19.62; Cl = 33.17.

All attempts to prepare the chloroderivative of benzoylbiuret were unsuccessful. It appears that the increment of the acidic nature of the substance by a substitution of the benzoyl group has interfered with the formation of the chloroderivative.

The chloroderivative of other substituted biurets are in the course of preparation, as also other substituted nitrogen chlorides.

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## CONTRIBUTIONS TO THE KNOWLEDGE OF HALOGENATION.

### VIII. NEW SERIES OF CHLOROXY COMPOUNDS.

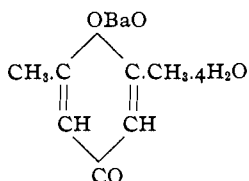
#### THE HYDROLYTIC CHLORINATION OF DIMETHYL- PYRONE. THE ISOLATION OF 2,6-DICHLORO- HYDROXY-3,5-DICHLORO-4-KETOHEPTANE AND ITS DECOMPOSITION INTO 3,5- DICHLORO-2,4,6-TRIOXYHEPTANE.

By RASIK LAL DATTA AND SATYARANJAN DAS GUPTA.

Received January 12, 1915.

The chlorination of dimethylpyrone has been effected by a variety of reagents. Chlorine has been found quite satisfactory to effect the change, although potassium chlorate and hydrochloric acid and also aqua regia, which give chlorine in the nascent state, can effect the chlorination of dimethylpyrone with the taking up of a water molecule and the opening of the pyrone ring.

The action of barium hydrate on 2,6-dimethylpyrone<sup>1</sup> presents a close analogy to the case in question. When an aqueous solution of dimethylpyrone is boiled with baryta water, there separates an insoluble barium salt, containing four molecules of water of crystallization,



When this salt is dissolved in hydrochloric acid and the resulting solution is extracted with ether, diacetylacetone is formed. By the removal of barium as barium chloride, the hypothetical dihydroxy compound is first formed, thus:

<sup>1</sup> Feist, *Ann.*, 257, 276 (1890).