confined in the bottle. The above equation necessitates the liberation of nitrogen which could not be detected under the above circumstances.

It is important to note here that just as the pseudohydrolysis of benzylamine gives benzyl alcohol, so the hydrolysis of benzylmonochloro- and benzyldichloroamines should give benzaldehyde and benzoic acid, respectively, an anticipation clearly verified by the above study of their decomposition products.

My thanks are due to Professor P. C. Ray, for his encouragement in carrying on the above investigation.

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To avoid delay, the equation given above has been published as it reads in Mr. Datta's manuscript. It seems altogether probable that the hydrolysis of the two chlorobenzylamines takes place in accordance with the following reactions:

$$C_6H_5CH_2NHCl + H_2O = C_6H_5COH + NH_4Cl$$
$$C_6H_5CH_2NCl_2 + 2H_2O = C_6H_5CO_2H + NH_4Cl + HCl$$

This rather unusual hydrolysis is occasioned by the fact that the chlorine in these chloroamines is positive but in the hydrolysis becomes negative, as in the hydrolysis of nitrogen trichloride.[1] Mr. Datta has apparently overlooked the fact that Professor Behal and his coworkers have recently used chlorourea as a chlorinating agent.[2] EDITOR.

SOME DERIVATIVES OF CHOLINE.

[SECOND PAPER.][3]

BY R. R. RENSHAW.

Received September 6, 1912.

The investigation to be described deals in part with the work done in an attempt to get an easily prepared derivative of choline that would serve as a starting point in the preparation of certain compounds, the properties of which might throw some light on the constitution of the phosphatides.

Iodocholine Iodide, $ICH_2CH_2N(CH_3)_3I$.—This substance has been obtained by Baeyer[4] and Schmidt[5] by the action of hydriodic acid on neurine. Baeyer also obtained it by heating iodine, red phosphorus and choline in sealed tubes for an hour at 120–50°, and Hundeshagen,[6] in small amount,

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[1] See Seliwanoff, *Ber.*, 27, 1016; Hentschel, *Ibid.*, 30, 1436; Noyes, THIS JOURNAL, 23, 462.

[2] See *Compt. rend.*, 153, 681 and 1229.

[3] Presented at the Indianapolis meeting of the American Chemical Society, June 29, 1911.

[4] *Ann.*, 140, 306 (1866).

[5] *Ibid.*, 267, 300 (1897).

[6] *J. prakt. Chem.*, 28, 245 (1883).

by the action of strong hydriodic acid on choline chloride. Schmidt[1] tried the action also of trimethylamine on ethylene iodide in alcoholic solution at 50° for several hours. The reaction mixture yielded only a small amount of the iodocholine iodide, some trimethyl ammonium iodide, and a dark brown filtrate, which was not investigated.

Even if only a moderate yield could be obtained by altering this latter addition process, it would still be a preferable method on account of the simplicity and directness of the procedure. With this thought in mind, it was decided to seek some modification which would improve the method. It had been shown by the author[2] previously that liquid trimethylamine and anhydrous ethylene chlorhydrin react practically quantitatively, forming choline chloride. The use of the liquid amine in this case seemed to be far superior to the use of the alcoholic solution, or of any other method of bringing about the reaction.

WITH F. G. FLOOD.

Twenty grams of recently purified ethylene iodide and approximately 4.2 grams of liquid trimethylamine were sealed in a bomb tube. The reaction began as the tube reached the room temperature, the crystals turning dark red. On opening the tube after heating 18 hours at 45° to 50°, some pressure due to trimethylamine was found. The reaction product was washed three times with boiling ether to remove the ethylene iodide, then treated with acetone, which dissolved out a considerable quantity of a dark brown material that was later shown to consist for the most part of the periodide of iodocholine iodide. There was left from the acetone extraction a small amount of an orange colored product melting, after several recrystallizations from alcohol, at 230° (uncorr.). This was undoubtedly iodocholine iodide. The yield was very small.

The reaction of trimethylamine and ethylene iodide was then carried out in different solvents at varying temperatures. Absolute alcohol, ether, gasoline and toluene were used. In most instances, particularly with temperatures above 50° and with alcohol under all conditions, considerable quantities of the periodide were formed. A yield of 70% of iodocholine iodide was finally obtained by allowing molecular quantities of the materials dissolved in toluene to stand six to eight days in sealed tubes. After the tube had stood a few hours, the iodide began slowly to separate out as a cream colored, flocculent mass. It was purified by recrystallizing from hot alcohol, or better from hot water. Thus procured, the iodide melts at 237.5° (corr.). Schmidt obtained a melting point of 230–31° for this substance.

Periodide of Iodocholine Iodide, $ICH_2CH_2N(CH_3)_3I—I_2$.—The dark brown material mentioned in the preceding, and formed whenever a mix-

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[1] *Loc. cit.*

[2] R. R. Renshaw, THIS JOURNAL, **32**, 128 (1910).

ture of trimethylamine and ethylene iodide are heated alone or in solution, was recrystallized from hot alcohol until a constant melting point of 160–61° (corr.) was obtained. It was then analyzed:

Calculated for $C_5H_{13}NI_4$: N, 2.36%. Found: N, 2.56% and 2.48%.

This periodide crystallizes from alcohol and acetone in long, shining needles of a dark reddish brown color. It is very soluble in acetone and in hot ethyl acetate; moderately soluble in hot alcohol and nearly insoluble in ether, chloroform, carbon tetrachloride, cold toluene, gasoline and in water. Boiling the periodide with water, or its solutions in alcohol or in acetone, gradually decomposes it with the formation of iodocholine iodide. This decomposition can be brought about very readily by warming with sodium carbonate solution. It might be thought that the use of this reaction, in conjunction with the procedures in which considerable quantities of the periodide were formed, would be a desirable method for preparing the iodide, but this is not so. The toluene method is preferable.

The periodide is readily obtained by adding a chloroform solution of iodine to an alcoholic solution of iodocholine iodide.

Iodocholine Nitrate, $ICH_2CH_2N(CH_3)_3NO_3$.—This substance was obtained by double decomposition of iodocholine iodide with silver nitrate, and purified by recrystallization from absolute alcohol. It crystallizes from that solvent in thin, shining plates that have an indistinct melting point. They soften at 177° and are finally completely melted at 183.5° (corr.). The nitrate is very soluble in cold water and in alcohol, somewhat soluble in acetone, and nearly insoluble in ether, benzene, gasoline and in carbon tetrachloride.

Calculated for $C_5H_{13}O_3N_2I$: N, 10.15%. Found: N, 10.35%.

The iodocholine nitrate was heated for 12 hours with silver glyceryl phosphate in aqueous solution. A gradual, though incomplete, precipitation of silver iodide, mixed with some silver phosphate, occurred. From the reaction mixture there was obtained, besides, some of the beginning materials, choline phosphate and glycerol. Heating the iodocholine nitrate with silver glyceryl phosphate has the same effect as heating iodocholine iodide with a dilute solution of silver nitrate. It has been found that under the latter conditions choline nitrate is obtained. The nitric ester produced is hydrolyzed approximately as soon as formed.

$$ICH_2CH_2N(CH_3)_3I + AgNO_3 \longrightarrow NO_3CH_2CH_2N(CH_3)_3NO_3 + H_2O \longrightarrow HOCH_2CH_2N(CH_3)_3NO_3 + HNO_3.$$

WITH B. M. MACBRIDE.

Bromocholine Bromide, $BrCH_2CH_2N(CH_3)_3Br$.—This compound has been prepared by Hofmann,[1] Bode[2] and Kruger and Bergell[3] by the ac-

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[1] *Jahresb. Chem.*, 11, 338 (1858).

[2] *Ann.*, 267, 268 (1892).

[3] *Ber.*, 36, 2901 (1903).

tion of trimethylamine on ethylene bromide under different conditions. A better method is described in the following experiment:

Molecular quantities of liquid trimethylamine and ethylene bromide were sealed in bomb tubes and heated for eight hours at 70–80°. By this time the contents of the tubes had apparently completely crystallized. The crystals were washed twice with ether and recrystallized once from alcohol, giving a product which was fairly pure. The yield was 90% of the theory. The bromide was recrystallized from alcohol until a constant melting point of 235.5° (corr.) was obtained. Bode[1] obtained a melting point of 230° (uncorr.).

The properties of this substance have been partially given by previous workers, particularly Bode. It may be added that the bromide is very soluble in water and in alcohol, moderately soluble in amyl alcohol, slightly soluble in acetone, and practically insoluble in benzene, gasoline, carbon tetrachloride and in chloroform.

Bromocholine Nitrate, $BrCH_2CH_2N(CH_3)_3NO_3$.—This substance was obtained by the action of silver nitrate on the corresponding bromide. It was purified by a number of reprecipitations of its alcoholic solution with ether. The nitrate gives no definit melting point, but softens and begins to decompose at 194°, and is finally completely melted at 200° (corr.). From alcohol it crystallizes in large needle-like plates, which are somewhat hygroscopic. It is very soluble in water and in alcohol, fairly soluble in hot amyl alcohol, slightly soluble in acetone, and practically insoluble in gasoline, benzene, ether, carbon tetrachloride and in chloroform.

Calculated for $C_5H_{13}O_3N_2Br$: N, 12.22%. Found: N, 12.13.

Action of Silver Hydroxide on Bromocholine Bromide.—Bode[2] has shown that when an excess of moist silver oxide acts on bromocholine bromide neurine is readily formed.

$$BrCH_2CH_2N(CH_3)_3Br + Ag_2O = CH_2{=}CHN(CH_3)_3OH + 2AgBr.$$

That the hydrobromic acid is very easily split out from the ethylene radical was shown in the following experiment: Four grams of bromocholine bromide dissolved in water were treated with two grams of silver oxide (equivalent to a little more than one molecular quantity of silver hydroxide). The silver oxide was carefully prepared free from carbonate and in the experiment carbon dioxide from the air was excluded. The reaction mixture was stirred a short time, filtered, and the water rapidly evaporated under diminished pressure. The neutral, hygroscopic residue was purified by several precipitations from its alcohol solution with ether. Melting point, 194° (uncorr.). Bode obtained 193° (uncorr.) for the melting point of neurine bromide. The substance reduced alkalin permanganate and otherwise showed the properties of that compound.

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[1] *Loc. cit.*

[2] *Ibid.*, p. 274.

$$BrCH_2CH_2N(CH_3)_3Br + AgOH \longrightarrow BrCH_2CH_2N(CH_3)_3OH + AgBr,$$

and

$$BrCH_2CH_2N(CH_3)_3^+ + OH^- \longrightarrow CH_2{=}CHN(CH_3)_3^+ + Br^- + H_2O.$$

Neurine iodide was obtained in a similar manner from iodocholine iodide.

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[FROM THE LABORATORY OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

VOLATIL FATTY ACIDS AND ALCOHOLS IN CORN SILAGE.

BY E. B. HART AND J. J. WILLAMAN.

Received August 30, 1912.

When green herbage of any kind is put into a silo, certain physical and chemical changes are noticed. There is a considerable rise in temperature, evolution of gases, a decrease in true protein and in carbohydrates, and a marked increase in acidity and aroma. The causes of these changes in corn have been studied in some detail by several investigators, principally by Burrill and Manns,[1] Babcock and Russell,[2] and E. J. Russell,[3] of England. As this paper deals only with the volatil fatty acids and alcohols, the work already done on them will be briefly reviewed.

The first to state the cause of the increase of acidity was Burrill, in 1888. He explained it all by bacterial action. He found many species of bacteria in the silage, and from what was known at that time of the action of bacteria, he concluded that all the acids in the silage were formed by the microbic decomposition of the carbohydrates in the fodder. He called the non-volatil acid lactic, and the volatil, acetic. He said there was no ethyl alcohol present, but probably butyl, although he made no definite analyses. He found great numbers of the yeast *Saccharomyces mycoderma* Rees, but concluded it formed no alcohol, as it does so only under certain conditions not found in the silo. In 1900 Babcock and Russell made extensive laboratory experiments on ensiling fodder. They showed quite conclusively that the major changes in corn silage formation were due to direct respiration of the living cells, and to intra-molecular respiration. They made silage under antiseptic conditions by the use of chloroform, ether or benzene, and found it perfectly normal, even to the characteristic silage aroma. They noticed that the acids and aroma were formed within a couple of days after ensiling the material, and before bacteria would have time to work to any extent.

The conclusions of Babcock and Russell were corroborated in 1908 by E. J. Russell at the Rothamsted station. He found that the volatil

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[1] Ill. Expt. Sta., *Bull.* 7 (1888).

[2] Wis. Agric. Expt. Sta., *Seventeenth Ann. Rpt.*, 1900.

[3] *J. Agric. Sci.*, 2 (1907–8).