THE ACTION OF CHLORINE ON ETHYL CARBAMIC ESTER. THE ISOLATION OF ETHYLMONOCHLOROCARBAMIC ESTER AND ITS BEHAVIOR TOWARDS AMINES AND ACID AMIDES.

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The action of chlorine on carbamide and substituted carbamides was studied by Chattaway, who succeeded in preparing their various chloroderivatives. He prepared a dichloroderivative of carbamide by passing a current of chlorine through a well cooled, saturated solution of this compound.[1] Behal and Detauf[2] prepared monochlorocarbamide by passing a calculated amount of chlorine over carbamide and separating the monochlorocarbamide from carbamide hydrochloride, which is formed along with it, by cooling with methyl chloride. The other theoretically possible chloroderivatives have not as yet been prepared. Chattaway[3] tried the action of chlorine on alkyl and acyl substituted carbamides and was able to prepare the monochloro-, dichloro- and trichloroderivatives of the alkyl substituted carbamides and only the monochloroderivatives of the acyl substituted carbamides. The action of chlorine on phenylcarbamide[4] is interesting. In this case the chlorine atom not only takes the place of the hydrogen atom united to nitrogen, but also enters the phenyl radical; and he isolated, under different circumstances, no less than ten chloroderivatives from this body. The action of bromine on carbamide has been studied by one of us,[5] but it does not give rise to any bromoderivatives, though there are evidences of the latter being formed in solution.

The ready substitution of the hydrogen atoms, united to nitrogen atom of carbamide, by chlorine, with the production of unstable substituted nitrogen chlorides, suggested to us the possibility of replacing similar hydrogen atoms by chlorine in analogous bodies. The action of chlorine on ethyl carbamic ester is first taken into hand with a view to prepare its monochloro and dichloroderivative, since the formation of this is strengthened by the fact that it may be considered as carbamide in which one amido group is substituted by an alkylated hydroxyl. In fact, the monochloroderivative has been isolated as a pale yellow oil. The action of chlorine on ethyl carbamic ester was studied by Schmidt,[6] evidently with a view to isolate the monochlorocarbamic ester. But he failed to obtain the same and prepared instead a condensation product of urethane with

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[1] *Proc. Roy. Soc.*, (*A*) **81**, 381 (1908).

[2] *Compt. rend.*, **53**, 381 (1911).

[3] *J. Chem. Soc.*, **95**, 129 (1909).

[4] Chattaway, *Ibid.*, **97**, 292 (1910).

[5] Datta, *Ibid.*, **101**, 166 (1912).

[6] *J. prakt. Chem.*, [2] **24**, 120 (1881).

dichloroacetaldehyde, *viz.*, dichloroethylidene-urethane, by allowing chlorine to act on the ester at a temperature ranging between 90–100°. The action that takes place, in this case, is quite different from what is expected for the formation of the chloroderivative. The urethane is first decomposed and the alkyl radical becomes simultaneously chlorinated and oxidized, forming dichloroacetaldehyde, thus:

$$NH_2COOC_2H_5 + 3Cl_2 = CHCl_2.CHO + COCl_2 + NH_4Cl + HCl$$

which in turn further condenses with two molecules of the ester to form dichloroethylidene-urethane, thus:

$$CHCl_2CHO + 2NH_2COOC_2H_5 = CHCl_2.CH(NHCOOC_2H_5)_2 + H_2O.$$

Now, it has been found that if, instead of chlorinating the substance at the high temperature employed by Schmidt, the substance be chlorinated in well cooled aqueous solution, the monochlorocarbamic ester could be isolated very easily as a pale yellow oil. The preliminary experiment for the chlorination was carried out with a perfectly saturated and well cooled solution of urethane, with the view that the chloroderivative might be precipitated, similarly to dichlorocarbamide, by passing a current of chlorine through a saturated solution of carbamide. But, contrary to expectation, no such precipitate came out even after passing the current of chlorine for a good length of time, though the solution showed signs of considerable absorption of it. The only change that was noticeable was that the solution assumed a yellow color. This fact might account for the inability of Schmidt, who studied the action of chlorine on ethyl carbamic ester as pointed out before, to isolate the real compound.

Now, on pouring the resulting yellow solution into water, a pale yellow oil, which showed quite active properties, separated and sank to the bottom. Its action on potassium iodide resulted in the liberation of iodine, and it acts as a vigorous chlorinating agent. It was suspected to be the monochloroderivative of the ester and that was found to be the case.

The chloro compound is most conveniently prepared thus: A dilute aqueous solution of ethyl carbamic ester is taken and a current of chlorine is passed into it, when, within a very short time, a pale yellow oil separates at the bottom. The passing of chlorine is continued till the oil ceases to absorb it, that is, until no further deepening of the yellow color of the oil takes place. It has to be noticed that the oil separates from solutions which are dilute, while from saturated solutions no separation takes place until water is added to it. It is for this reason that a dilute solution and not a saturated one has to be employed. The oil is next separated by means of a separating funnel, washed with water and dried, when it is obtained as a pale yellow oil. If the oil be analyzed by separating it directly without washing, the percentage of chlorine comes out a trifle high, which is due to some chlorine dissolved in the oil. Like the nitrogen halogen derivatives, the chlorine in this is estimated by adding the oil to excess of potassium iodide solution and titrating the iodine liberated with sodium thiosulfate. Also a gravimetric halogen estimation was made according to Carius' method.

0.2535 g. liberated I = 20.3 cc. *N*/10 I; Cl as: NCl = 28.43%; 0.4163 g. gave 0.04773 AgCl; Cl = 28.3%; calc. for $C_3H_6O_2NCl$: Cl = 28.74%.

The action that takes place is one of substitution, involving the liberation of one molecule of hydrochloric acid for each molecule of the ester chlorinated.

$$NH_2COOC_2H_5Cl = NHCl.COOC_2H_5 + HCl.$$

Since urethane is not a base, the liberated hydrochloric acid does not interfere with the chlorination of this substance and hence the compound is produced quantitatively, whereas in the case of the chlorination of dichlorocarbamide the liberated hydrochloric acid holds bound two-thirds of the urea employed as urea hydrochloride, and nearly one-third of the theoretical yield is obtained as pointed out before by one of us.[1]

The compound is a pale yellow, moderately viscous oil, having a refractive index of 1.44235 at 30°. It is tolerably stable, and during the chlorination no appreciable amount of hydrolysis takes place. The substance decomposes very slowly when kept in stoppered bottles; when kept in contact with water for some days, it yields a white crystalline substance which is under examination. The compound boils at about 99°, giving out bubbles of gas, evidently due to the decomposition of the compound. If the oil be heated to 140° and then allowed to cool, a solid substance begins to separate from the liquid and the stem of the tube is filled with a white, solid substance in the form of a sublimate. If it be heated in a bulb tube, a sudden rush of white vapors come out of the tube, which deposit on the upper part of the tube. On further heating, the whole thing chars, leaving a deposit of carbon. The composition of the solid which separates from the heated oil is also under investigation. The substance has a pungent smell, similar to chlorocarbamides. It has a remarkably corrosive and painful action on the skin; when applied to the skin a very painful sensation is felt in the course of a few minutes, which increases, gradually turning the skin violet-black. If the action be prolonged for some time, very painful and deep-seated scars are formed.

The compound is an extremely energetic agent, like dichlorocarbamide. But it has a great advantage over the latter, which has a great tendency of being hydrolyzed in the process of chlorination; this compound, however, effects chlorination smoothly and without the least amount of hydrolysis. For instance, in the chlorination of the lower aliphatic amines there is a vigorous hydrolysis with dichlorocarbamide; whereas the reaction takes place very smoothly and without the least hydrolysis with

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[1] Datta, *J. Chem. Soc.*, **101**, 166 (1912).

this body. So the reagent promises to be of signal service in cases of chlorination where free chlorine in not suitable, and where hypochlorous acid or dichlorocarbamide is too vigorous an agent effecting rapid hydrolysis. The chlorination of benzylamine was studied in detail as representing the amines, and that of benzamide, as representing the acid amides. It was also found that acetone interacts vigorously with it, forming a chloro compound. Its action on such bases as piperazine and hexamethylenetetramine is very interesting, and instead of chloroderivatives other condensation products, containing no halogen, are formed. These will be described in a future communication.

The Action of Ethylchlorocarbamic Ester on Benzylamine.—The chlorination of benzylamine was effected by means of dichlorourea by one of us,[1] producing both monochloro- and dichlorobenzylamines. It has now been found that, by the action of the chloroester, both monochloro- and dichlorobenzylamines could be prepared according as the one or the other be employed in excess. For preparing monochlorobenzylamine, the chlorourethane is added to excess of benzylamine and the resulting product is treated with water, when the excess of amine dissolves in it, leaving monochlorobenzylamine as a pale yellow viscous oil. It was separated and dried as usual. Its identity was established by a halogen estimation.

0.2531 gave 0.2539 AgCl; Cl = 24.80%; calc. for $C_6H_5CH_2NHCl$: Cl = 25.08%.

The dichloro compound is prepared very easily by adding excess of ethylchlorocarbamic ester to benzylamine and then washing with water the pale yellow oil which separates. A halogen estimation in the dried substance proved the identity of the compound.

0.2160 gave 0.3505 AgCl; Cl = 40.15%; calc. for $C_6H_5CH_2NCl_2$: Cl = 40.34.

The Action of Ethylchlorocarbamic Ester on Benzamide.—Benzamide could hitherto be chlorinated by means of sodium hypochlorite.[2] It has been recently shown[3] that chlorination in aqueous suspension is possible for the production of the monochloroderivative. The present chlorination by the chlorocarbamic ester is an addition to the methods of chlorination of benzamide. The chlorination of benzamide is effected most conveniently thus: Ethylchlorocarbamic ester is added to finely powdered benzamide with a small quantity of water. After allowing the reaction mixture to stand for some time, the chlorination becomes complete and the product is washed with water and recrystallized therefrom. Its melting point was found to be 116°, which is evidently of pure benzoylchloroamide.

The action of bromine on urethane in conjunction with soda was studied

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[1] Datta, THIS JOURNAL, **34**, 1613 (1912).

[2] Bender, *Ber.*, **15**, 410 (1882).

[3] Datta and Ghosh, THIS JOURNAL, **35**, 1044 (1913).

by Hantzsch,[1] and he obtained the dibromoderivative, four molecules of which are united chemically with a molecule of sodium bromide to form ethylic dibromoamidocarboxylate sodium bromide, $4NBr_2COOC_2H_5$, NaBr, as a yellow granular powder the sodium bromide of which is firmly in union and cannot be removed by washing with water. It is most likely that the constitution of this body is quite different from what has been assigned to it by Hantzsch. In all probability it has a complicated formula, as can be inferred from the unstable nature of the monochlorocarbamic ester as also from the less energy of bromine for reactions of this kind. It might be a condensed compound having the formula given below:

$$4(NBr_2.COOC_2H_5)NaBr = \underset{\substack{|\\ COOEt}}{Br.N.Br_2} - \underset{\substack{|\\ COOEt}}{NBr_2} - \underset{\substack{|\\ COOEt}}{NBr_2} - \underset{\substack{|\\ COOEt}}{NBr_2Na}$$

The formation of such a compound may be explained thus: Bromine acting on urethane in conjunction with soda forms NaBrNCOOEt, analogous to the formation of potassium acetobromoamide by the action of bromine and caustic potash on acetamide. Now this further adds two atoms of bromine to form $NBr_3NaCOOEt$, making the nitrogen pentavalent. Four molecules of this condense, with the elimination of sodium bromide, to form the above compound.

$$4NBr_3NaCOOEt = 3NaBr + 4NBr_2COOEt, NaBr.$$

We are at present engaged in preparing the chloroderivatives of other esters of chlorocarbamic acid and also of alkyl and acyl substituted carbamic esters.

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ACYL DERIVATIVES OF o-AMINOPHENOL.

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In an extended piece of work published some years ago the senior author[2] found that when *o*-nitrophenylethylcarbonate is reduced with tin and hydrochloric acid a urethane is obtained soluble in bases and evidently having the carbethoxy radical attached to nitrogen. By modifying the conditions, a basic substance was isolated in which the carbethoxy radical is attached to oxygen. On standing, this rapidly changes to the urethane. The same urethane was obtained from *o*-aminophenol and chlorocarbonic-ethylether in ether solution. A similar rearrangement

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[1] *Ber.*, 27, 1248 (1894).

[2] *Am. Chem. J.*, 23, 1.