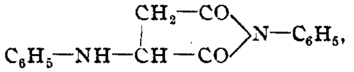
Summary.

Aniline and fumaric or maleic acid form phenylaminosuccinphenylimide,



$$\begin{array}{l}\qquad\qquad\quad \mathrm{CH_2{-}CO}\diagdown \\ \qquad\qquad\quad\ |\qquad\qquad\ \ \mathrm{N{-}C_6H_5,} \\ \mathrm{C_6H_5{-}NH{-}CH{-}CO}\diagup\end{array}$$

in the production of which two reactions are concerned, namely, one leading to the formation of the imido ring and the other involving addition of the amine. A further study of these reactions has led to the following results:

1. Other primary amines, such as β-naphthylamine, the three toluidines, xylidine, benzidine, benzylamine and *p*-phenetidine, resemble aniline in their behavior with fumaric acid; whereas tribromoaniline, *p*-bromoaniline and methyl- *p*-aminobenzoate fail to react.

2. The indications are that these two reactions take place in sequence and are not concurrent, since the addition of amines seems to be dependent on the imido ring. But for the present we cannot decide whether addition is due to the imido ring, to maleinoid configuration, or to both causes, until we have examined maleinoid compounds containing no imido ring. It is quite evident, however, that most fumaroid compounds cannot add amines.

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THE PREPARATION AND DECOMPOSITION OF BENZYLMONOCHLORO- AND BENZYLDICHLOROAMINES.

BY RASIK LAL DATTA.

Received September 14, 1912.

The interaction of both aliphatic and aromatic amines was studied in brief in a paper to the Chemical Society,[1] when it was shown that dichlorocarbamide is essentially a chlorinating agent, behaving analogously to hypochlorous acid. The products of the interaction of dichlorourea with amines are both monochloro and dichloro derivatives with the primary ones and monochloro with the secondary ones. The chlorination proceeds quietly without the least amount of hydrolysis with the higher members, while, with the lower members the chlorination is accompanied by brisk hydrolysis resulting in the evolution of gases. The reaction was specially studied with benzylamine, which according to the proportions of dichlorourea gave both benzyl monochloro- and benzyldichloroamines.

The original method of obtaining these chloroamines depends upon the action of sodium or calcium hypochlorite on amines.[2] In fact this was the only method known and the present method is next to it in simplicity,

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

[2] Berg, *Compt. rend.*, **116**, 327 (1893).

yielding, however, a purer product. In order to prepare the monohalogen derivative, it is the benzylamine which has to be kept in excess while the reverse must be the method in the preparation of dichloro derivative. In both cases, the reaction takes place almost quantitatively, unaccompanied by the least hydrolysis. To ensure the latter, the operation is conducted in the cold.

The chief interest lies in the spontaneous decomposition under water of benzylmonochloroamine, a viscous liquid, which is conveniently extracted with ether from the reacting mixture of dichlorourea and benzylamine. A portion of this viscous liquid was kept under water in order to ascertain whether slow but persistent hydrolysis does take place with the lapse of time. It was noticed, however, in a few days that the viscosity had greatly diminished. This led to a suspicion, the reason of which was not far to see, as a distinct smell of benzaldehyde was noticed. The now mobil layer of liquid underneath the water was separated by means of a separating funnel and was found on examination to be pure and simple benzaldehyde. Thus benzylmonochloroamine undergoes quantitative hydrolysis to benzaldehyde.

Benzyldichloroamine is obtained by the above method by adding an excess of dichlorourea to benzylamine. This compound is less viscous than the monochloro derivative and is capable of being conveniently separated by a separating funnel. It is much more stable than the monochloro derivative and, on keeping it under water as before, at first no appreciable hydrolysis seemed to take place, for the valuation of halogen after the lapse of some days, showed that the substance had remained intact.

0.3474 gave 0.5470 AgCl: Cl = 38.95. Calc. for $C_6H_5.CH_2.NCl_2$: Cl = 40.34.

It was seen, however, that after the lapse of a long time hydrolysis had indeed, taken place, benzaldehyde being, as before, a product. Thus benzyldichloroamine decomposes also into benzaldehyde, but the completion of the hydrolysis takes a considerable amount of time, since the hydrolysis goes on exceedingly slowly.

On the other hand, if benzyldichloroamine be left in a stoppered bottle for a few days, it is found that small crystals make their appearance at the sides of the bottle in contact with the liquid. On opening the stopper, a pressure was felt from within, and besides the smell of this compound, a distinct smell of free chlorine was noticed. The bottle was stoppered again and allowed to remain, the pressure being released from time to time, the whole liquid being ultimately solidified into a mass of crystals, which on examination was found to be benzoic acid. The reaction is explainable according to

$$C_6H_5CH_2NCl_2\ O_2 = C_6H_5.COOH\ HCl\ N\ Cl$$

the oxygen required for the reaction being evidently obtained from air 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).