176. *Studies on Hydrogen Cyanide. Part XIV. Formamidodichloride.*

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Formamidodichloride is produced during the action of hydrogen chloride on hydrogen cyanide in which the final product is the crystalline dichloromethyleneformamidine hydrochloride (sesquichloride). An explanation is now offered for the mode of formation of the latter compound. The presence of formamidodichloride was established through its condensation with nitrobenzaldehydes, whereby nitrobenzylidenebisformamides were ultimately obtained, and the identity of these compounds was confirmed by synthesis from formamide.

It is only after hydrogen chloride has been passed for a long time into a solution of hydrogen cyanide in ether that any change becomes apparent by the deposition of the solid sesquichloride of hydrogen cyanide (Hinkel and Dunn, J., 1930, 1836; Hinkel, Ayling, and Beynon, J., 1936, 185). No explanation has hitherto been offered for the formation of the sesquichloride, but it is probably the result of several reactions in which the union of hydrogen cyanide with hydrogen chloride to form formimidochloride (I) may be the primary stage.

In order to account for the formation of the hydrochlorides of the formimido-ethers and the phenolic aldimines by the action of hydrogen chloride on hydrogen cyanide in the presence of alcohols and phenols, respectively, Pinner and Klein (*Ber.*, 1878, **11**, 1475) and Gattermann (*ibid.*, 1898, **31**, 1149) presumed the primary action to be the formation of formimidochloride. This compound has, however, not been isolated, and it would seem that, if it does exist in solution it readily decomposes into its components with increase in dilution, since dilute solutions of hydrogen cyanide and hydrogen chloride in equimolecular proportion can be kept for a long time without undergoing any apparent change. When resorcinol is added to such dilute ethereal solutions, a small amount only of the insoluble aldimine hydrochloride is deposited, indicating that very considerable decomposition of formimidochloride must have occurred, since with increase in concentration of one or both of the reactants the yield of aldimine hydrochloride is also much increased (see Tables I and II). With increase in the concentration of the two reactants, hydrogen cyanide and chloride, not only is there an apparent increase in formimidochloride but further changes also occur, since some crystalline " sesquichloride," which is insoluble in ether, begins to be deposited. The greater the concentration, the greater the yield of the sesquichloride.

Since the formation of the sesquichloride requires two molecules of hydrogen cyanide for three molecules of hydrogen chloride, the supernatant liquid becomes relatively richer in hydrogen cyanide; nevertheless, there is always free hydrogen chloride in solution and the formation of the sesquichloride is never complete. Furthermore, complete formation of the sesquichloride does not occur when the original proportion of hydrogen cyanide to hydrogen chloride is 2 : 3 or even more.

The changes occurring with increase in the concentration of formimidochloride cannot be primarily a simple union of two molecules of the latter to give chloromethyleneformamidine (II) as below, since this compound does not further combine with hydrogen chloride (cf. Hinkel and Dunn, *loc. cit.*).

$$\text{(I.)}\quad 2\mathrm{NH{:}CHCl} = \mathrm{NH{:}CH{\cdot}N{:}CHCl}\ \text{(II.)}\quad + \mathrm{HCl}$$

The existence of two chlorine atoms on the terminal carbon atom of the sesquichloride therefore suggests formamidodichloride, dichloromethylamine (III), to have been formed at one period. The existence of that compound would readily account for the formation of the sesquichloride through the union of two of its molecules :

$$\text{(III.)}\quad 2\mathrm{NH_2{\cdot}CHCl_2} = \mathrm{NH_2{\cdot}CHCl{\cdot}NH{\cdot}CHCl_2} + \mathrm{HCl}$$

Several examples of the existence of amidodichlorides and their derivatives exist among aromatic compounds (Wallach, *Annalen*, 1877, **184**, 4; Pinner and Klein, *Ber.*, 1879, **12**, 97). These amidodichlorides in general are unstable substances which are transformed into imidochlorides by loss of hydrogen chloride. On the other hand, several substituted imidochlorides are known which unite directly with halogen halides, yielding crystalline dihalogen amides (Stephen and Bleloch, J., 1931, 888; Lander and Law, J., 1904, **85**, 1695; Franzen and Henglein, *J. pr. Chem.*, 1915, **91**, 245). A crystalline acetamidodichloride has also been prepared by the action of hydrogen chloride on acetonitrile (unpublished work).

The presence of formamidodichloride was made evident through its condensation product with the nitrobenzaldehydes, since it has been shown (Reich and Richben, *Monatsh.*, 1904, **25**, 933) that amides react with aldehydes, giving rise to three classes of derivative (IV, V, VI) according to the conditions employed.

$\mathrm{R{\cdot}CH{:}N{\cdot}COR'}$ (IV.)

$\mathrm{R{\cdot}CH(OH){\cdot}NH{\cdot}COR'}$ (V.)

$\mathrm{R{\cdot}CH(NH{\cdot}COR')_2}$ (VI.)

$\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH(NH{\cdot}CHCl_2)_2}$ (VII.)

$\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH(NH{\cdot}CHO)_2}$ (VIII.)

$\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}CHO}$ (IX.)

The condensation products of formamidodichloride could not be isolated in the pure state owing to their instability, but they appear to be of the type (VI) and to possess the structure (VII), since on carefully regulated hydrolysis they yielded the corresponding *nitrobenzylidenebisformamides* (VIII). The identity of these bisformamides was confirmed by their synthesis from the corresponding nitrobenzaldehydes and formamide (cf. Ytterah and Pandy, *Proc. Indian Acad. Sci.*, 1942, **15**, *A*, 256).

No condensation occurs between the nitrobenzaldehydes and formamide in benzene, dioxan, or alcoholic solution, but does so readily when formamide is replaced by its hydrochloride. Under these conditions the bisformamides of *m*- and *p*-nitrobenzaldehydes have been obtained, m. p. 178° and 192°, respectively. Ytterah and Pandy (*loc. cit.*) give the m. p. of the *m*-derivative as 168° but it is doubtful whether they obtained the pure compound, since *m*-nitrobenzaldehyde, when heated with formamide under the conditions described by them, yields a monoformamide (IX), m. p. 158°.

The bisformamido-compounds are very readily hydrolysed by dilute acids even in the cold. The *p*-derivative presents an unusual feature, for, whenever obtained from formamidodichloride, the specimen, even after several recrystallisations, melts at 192° to a clear colourless liquid. On being kept for many weeks, the compound gradually changes into a *dimer*, the m. p. slowly falling and being finally replaced by a decomposition point about 160° with the formation of a deep red product. When synthesised from formamide hydrochloride, a crude specimen could be obtained, m. p. 192°, but this product more often than not would yield the dimer after one crystallisation.

EXPERIMENTAL.

Effect of Dilution on Aldimine Formation.—A solution of dry hydrogen chloride in dry ether was prepared (24 g. per 100 c.c.), and by its means four mixtures were prepared containing unimolecular quantities of hydrogen chloride, hydrogen cyanide, and resorcinol in various quantities of dry ether. The mixtures were kept at 0° for several hours, and then allowed gradually (18 hours) to reach 10°. After the supernatant liquids had been poured off, the semi-solid deposits were washed with ether by decantation and dissolved in water. The aqueous solutions of the aldimine hydrochlorides were then hydrolysed by gentle boiling for 10 minutes, cooled, and extracted with ether. After the extracts had been dried and the ether removed, the residues of resorcylaldehyde were weighed.

TABLE I.

In each expt., 0·1 g.-mol. each of HCl (15 c.c. of solution), HCN (4 c.c.), and resorcinol (11 g.) was used. The calculated yield is 13·8 g.

Added ether, c.c.	74	54	34	4
Total vol., c.c.	100	80	60	30
Yield of aldehyde, g.	0·7	1·6	3·9	7·2

Effect of Excess of Hydrogen Cyanide on Aldimine Formation.—By means of an ethereal solution of hydrogen chloride containing 21 g. in 100 c.c., two solutions were prepared containing unimolecular quantities of hydrogen chloride and resorcinol with four molecular quantities of hydrogen cyanide at two different dilutions in ether, and for comparison a similar set was made employing unimolecular quantities of each reactant at corresponding dilutions. The conditions of the experiment and the method of analysis were as previously described.

TABLE II.

In each expt., 0·1 g.-mol. each of HCl (17 c.c. of solution) and resorcinol (11 g.) was used. The calculated yield is 13·8 g.

HCN, c.c. (equiv. to 0·1 g.-mol.)	16	16	4	4
Added ether, c.c.	0	10	12	22
Total vol., c.c.	40	50	40	50
Yield of aldehyde, g.	9·4	8·7	6·6	4·7

Condensation of Formamidodichloride with m-*Nitrobenzaldehyde.*—To a solution of *m*-nitrobenzaldehyde (15 g.; 1 mol.) in dry ether (35 c.c.) hydrogen cyanide (8·1 c.c.; 2 mols.) was added. The ice-cooled solution was saturated with hydrogen chloride, and the mixture left overnight, a thick viscous liquid separating. The supernatant ether was decanted, the semi-solid residue washed with ether, triturated with a little crushed ice and water, and the solid thus formed, filtered off and washed with alcohol and then with benzene. The product was dried in air and crystallised from hot alcohol; m. p. 178°, unchanged by admixture with a synthesised specimen of m-*nitrobenzylidenebisformamide* (Found: C, 48·5; H, 3·9; N, 18·85. $C_9H_9O_4N_3$ requires C, 48·4; H, 4·0; N, 18·8%) (see below).

m-*Nitrobenzylidenebisformamide.*—A solution of *m*-nitrobenzaldehyde (5 g.; 1 mol.) and formamide (10 g.; 6 mols.) in ether (20 c.c.) was saturated with hydrogen chloride at 0°. The resulting thick liquid was left overnight, and then gently warmed on the water-bath to decompose the excess of formamide. The solid deposit of ammonium chloride so formed was removed, and the filtrate evaporated to semi-dryness on the water-bath, during which much hydrogen chloride was evolved. The solid was triturated with a few c.c. of ice-water and washed with alcohol, followed by ether. The crude product melted at 166—175° and was crystallised from hot alcohol, yielding colourless prisms, m. p. 178° (Found: C, 48·2; H, 4·0; N, 18·5%).

Condensation of Formamidodichloride with p-*Nitrobenzaldehyde.*—Since *p*-nitrobenzaldehyde is only sparingly soluble in ether, the condensation was carried out in dioxan. Into an ice-cooled solution of *p*-nitrobenzaldehyde (7·5 g.; 1 mol.) and hydrogen cyanide (4 c.c.; 2 mols.) in dioxan (21 g.), hydrogen chloride was passed until the gain in weight was 11 g. (6 mols.), and the mixture left overnight. On addition of an excess of ether to the clear yellow liquid, a viscous liquid was precipitated. The supernatant liquid was decanted, and the viscous product redissolved in the minimum of dioxan and reprecipitated by ether. The semi-solid product was treated as in the previous experiment and crystallised from hot alcohol, *p*-nitrobenzylidenebisformamide being obtained as colourless crystals, m. p. 192° unchanged by admixture with an authentic specimen. After several weeks, the m. p. of the compound gradually fell to *ca.* 170°. The change was accelerated by repeated crystallisation from methyl alcohol–dioxan, transparent crystals being obtained which decomposed without melting at 160° with evolution of gas, forming a red solid of high m.p. [*M*, by Rast's camphor method, 462. $(C_9H_9O_4N_3)_2$ requires *M*, 458].

p-*Nitrobenzylidenebisformamide.*—Synthesised as for the *m*-compound except that the ether was replaced by 10 c.c. of dioxan, this compound melted at 192°, but unlike that prepared from formamidodichloride it was sensitive to change on crystallisation and often after one crystallisation was converted into the foregoing *dimer*.

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