149. *Studies on Hydrogen Cyanide. Part V. Reactions of Iminoformylcarbylamine.*

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IMINOFORMYLCARBYLAMINE (bimolecular hydrogen cyanide) was first obtained by Nef (*Annalen*, 1895, **287**, 337), and its constitution finally established by Hinkel and Dunn (J., 1930, 1836). According to Nef, the compound is converted into ammonium formate by heating with water at 100° under pressure; actually, hydrolysis occurs when the compound is dissolved in cold water, for ammonium formate is obtained on evaporation in a desiccator. This ready hydrolysis accounts for the discrepancy between the calculated and the actual analytical values for the compound described by Nef (*loc. cit.*) as the silver derivative of the hydrate of bimolecular hydrogen cyanide, C_2N_2HAg,H_2O, containing about 5% of adsorbed nitric acid. Nef prepared the derivative by mixing aqueous solutions of silver nitrate and bimolecular hydrogen cyanide, but no pure compound can be obtained in this way; the precipitates always contain nitrate in varying quantities and the composition varies with the concentration of the reactants and with the duration of time prior to filtration.

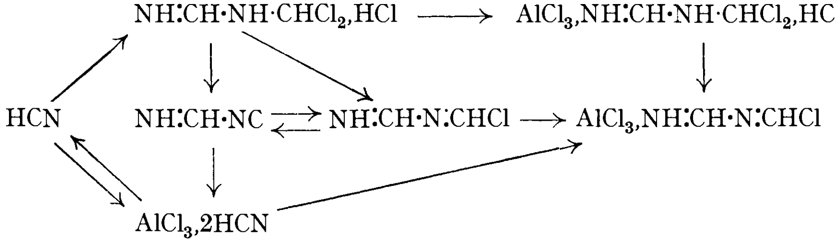
Iminoformylcarbylamine dissolves unchanged in absolute alcohol, and the addition of alcoholic silver nitrate, with either reactant in excess, leads to the formation of a white crystalline solid of constant composition, $2AgNO_3,5HCN$. This *compound* is slowly hydrolysed by cold water, in which it is slightly soluble, and explodes when heated.

Iminoformylcarbylamine in ethereal solution also forms with mercuric chloride a *compound* which, by analysis, corresponds to $HgCl_2,3HCN$ or more probably $2HgCl_2,3(HCN)_2$, since, with hydrogen chloride, it yields a deliquescent solid which appears to be the *compound* $2HgCl_2,3(2HCN,HCl)$. The latter reaction corresponds to the conversion of iminoformylcarbylamine, $NH{:}CH{\cdot}NC$, by means of hydrogen chloride into chloromethyleneformamidine, NH:CH·N:CHCl, as observed by Hinkel and Dunn (*loc. cit.*) instead of the formation of the sesquichloride as stated by Nef (*loc. cit.*).

Hydrogen cyanide unites with aluminium chloride to form the double compound $AlCl_3,2HCN$ (Hinkel and Dunn, J., **1931**, 3243; compare Perrier, *Comp. rend.*, 1895, **120**, 1424). In a similar manner, iminoformylcarbylamine yields a double compound, $AlCl_3,(HCN)_2$, and this is identical with the compound obtained by Hinkel and Dunn from hydrogen cyanide. It melts at 125° with decomposition into hydrogen cyanide and aluminium chloride and although prepared from iminoformylcarbylamine, the latter could not be regenerated from it. The decomposition also occurs at 100° but at a much slower rate. The double compound does not combine with hydrogen chloride at the ordinary temperature, but at 80° reaction occurs, again with only one molecule of hydrogen chloride (compare above), yielding the *compound* $AlCl_3$,NH:CH·N:CHCl, identical with that obtained by the direct union of aluminium chloride and chloromethyleneformamidine. This double compound yields *p*-tolualdehyde when heated with toluene in the presence of free aluminium chloride.

The sesquichloride of hydrogen cyanide (dichloromethylformamidine hydrochloride) also yields a *double compound*, $AlCl_3$,NH:CH·NH·$CHCl_2$,HCl, and this readily decomposes into $AlCl_3$,NH:CH·N:CHCl on heating. The decomposition also proceeds slowly in toluene at 100°, leading to the formation of a mixture of *p*-tolualdehyde and tolylhydrylformamidine hydrochloride. These two compounds result from the reaction on toluene of $AlCl_3$,NH:CH·N:CHCl and $AlCl_3$,NH:CH·NH·$CHCl_2$,HCl respectively (compare above and Gattermann and Schnitzpahn, *Ber.*, 1898, **31**, 1770).

The inter-relationship between hydrogen cyanide, iminoformylcarbylamine, and its hydrogen chloride derivatives and the double compounds with aluminium chloride is shown in the following scheme :



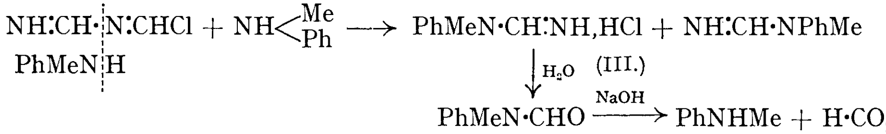
With aromatic primary amines, the sesquichloride of hydrogen cyanide and chloromethyleneformamidine both yield *NN'*-diarylformamidines (Dains, *Ber.*, 1902, **35**, 2496; Hinkel and Dunn, J., **1930**, 1836) and the first stage in each of these reactions may consist in the removal of hydrogen chloride by the base with the formation of iminoformylcarbylamine (I), which then reacts with the base to give the diarylformamidine (II).

$$\underset{\text{(I.)}}{NH{:}CH{\cdot}NC} \xrightarrow{R\cdot NH_2} NH{:}CH{\cdot}N{=}\!\vdots\!{=}CH{\cdot}NHR \xrightarrow{R\cdot NH_2} NH{:}CH{\cdot}NH_2 + \underset{\text{(II.)}}{RN{:}CH{\cdot}NHR}$$

In support of this view, iminoformylcarbylamine has been found to react with primary amines to yield the diarylformamidines.

Dimethylaniline reacts with the two hydrogen chloride derivatives of iminoformylcarbylamine (Gattermann and Schnitzpahn, *loc. cit.*; Hinkel and Dunn, *loc. cit.*) but not with iminoformylcarbylamine itself. The initial stage in the formation of crystal-violet leuco-base with the hydrogen chloride derivatives must be, therefore, not complete removal of hydrogen chloride as with primary amines, but elimination of the chlorine atom attached to the NC group with the *p*-hydrogen of the dimethylaniline.

In order to complete the sequence of the study of the behaviour of aromatic amines with these compounds, the reactions with the comparable secondary amine, monomethylaniline, have now been examined. Since there is only one amine hydrogen atom, a different type of reaction must occur. Iminoformylcarbylamine does not react with monomethylaniline, but chloromethyleneformamidine and the sesquichloride of hydrogen cyanide both yield N-*phenyl*-N-*methylformamidine hydrochloride* (III) when heated with the amine, indicating that the presence of the chlorine atom is necessary for the reaction, as in the case of dimethylaniline. The phenylmethylformamidine hydrochloride yields on hydrolysis, first, formylmethylaniline and, finally, monomethylaniline, a sequence similar to that obtained with benzhydrylformamidine hydrochloride by Gattermann and Schnitzpahn (*loc. cit.*).



$$\begin{array}{lll} \mathrm{NH{:}CH{\cdot}\vdots N{:}CHCl} + \mathrm{NH}{<}^{\mathrm{Me}}_{\mathrm{Ph}} & \longrightarrow & \mathrm{PhMeN{\cdot}CH{:}NH,HCl} + \mathrm{NH{:}CH{\cdot}NPhMe} \\ \mathrm{PhMeN\vdots H} & & \big\downarrow \mathrm{H_2O} \quad \mathrm{(III.)} \\ & & \mathrm{PhMeN{\cdot}CHO} \xrightarrow{\mathrm{NaOH}} \mathrm{PhNHMe} + \mathrm{H{\cdot}CO_2H} \end{array}$$

When hydrogen chloride is passed into a solution of iminoformylcarbylamine in alcohol, formamidine hydrochloride and ethyl orthoformate result : chloromethyleneformamidine is probably first produced, since this compound with alcohol also gives rise to the same products. This action is similar to that of the sesquichloride of hydrogen cyanide with alcohol (Claisen and Matthews, *Ber.*, 1883, **16**, 309) in which, in addition to the formamidine hydrochloride and ethyl orthoformate, some ethyl chloride is formed. These compounds can only result from the ready decomposition of the sesquichloride into chloromethyleneformamidine and hydrogen chloride.

EXPERIMENTAL.

Preparation of Iminoformylcarbylamine.—Owing to the vigour of the reaction between quinoline and the sesquichloride of hydrogen cyanide, the iminoformylcarbylamine prepared by Hinkel and Dunn's method (J., 1930, 1838) nearly always contains traces of quinoline and its hydrochloride. It was readily obtained pure by the following procedure. The reaction flask was attached to a horizontal steam-jacketed tube, which in turn was connected to a similar water-cooled tube, followed by a U-tube immersed in solid carbon dioxide and alcohol. The quinoline was slowly run into the flask containing the sesquichloride and, after the vigorous reaction had subsided, warm dry air was slowly drawn through the apparatus. The impurities condensed in the steam-jacketed tube, and pure iminoformylcarbylamine, m. p. 85°, condensed as prismatic crystals in the water-cooled tube. The strongly cooled U-tube served to collect the small quantity of iminoformylcarbylamine not previously condensed and the free hydrogen cyanide which is always formed in the reaction.

For the preparation of small quantities of the carbylamine (5 g.), the requisite amount of sodium cinnamate may conveniently be substituted for the quinoline. With either chloromethyleneformamidine or the sesquichloride, the pure carbylamine was thus obtained in over 80% yield.

Hydrolysis.—Iminoformylcarbylamine was dissolved in water, and the resulting acid solution shaken with ether. The latter yielded no original substance on evaporation in a vacuum. The aqueous solution was evaporated to dryness in a vacuum over sulphuric acid and after 48 hours a white crystalline solid was obtained, consisting of pure ammonium formate, m. p. and mixed m. p. 114° (Yield, 0·68 g. from 0·31 g.; 94%).

Chloromethyleneformamidine.—This was prepared by Hinkel and Dunn's method (*loc. cit.*), with the exception that the sesquichloride was mixed with powdered aluminium (3 atoms); after prolonged heating at 100° in a vacuum, aluminium alone remained.

Action of Silver Nitrate on Iminoformylcarbylamine.—(1) *In aqueous solution.* Silver nitrate (1·7 g.; 1 mol.) in ice-water (100 c.c.) was added to iminoformylcarbylamine (1·08 g.; 2 mols.) in ice-water (20 c.c.). The white crystalline deposit was quickly removed, washed with ice-water and then with ether, and dried in a vacuum over sulphuric acid [Found : Ag, 53·75; N (alkaline hydrolysis), 12·7; N as NO_3 (alkaline reduction, Devarda's alloy), 3·0. C_2HN_2Ag,H_2O requires Ag, 60·3; N, 15·6%] (Nef, *loc. cit.*, records Ag, 54·5; N, 16·5%).

If the precipitated silver salt was kept in contact with the solution for an hour or more before filtration, the silver and the nitrogen content both diminished. In all cases the crystalline solids obtained were somewhat soluble in water, contained nitrate, exploded when heated, and darkened on exposure to light, especially when moist.

(2) *In alcoholic solution.* Solutions of silver nitrate (1 mol.) and iminoformylcarbylamine (2 mols.) in absolute alcohol were mixed. The resulting precipitate was washed three times

with alcohol and dried in a vacuum over sulphuric acid. The white crystalline solid, which contained nitrate and gave the characteristic reaction with a solution of diphenylamine in sulphuric acid, could be kept unchanged in light, but rapidly darkened in contact with moisture [Found: Ag, 44·8; N (alkaline hydrolysis), 14·5; N as NO_3 (alkaline reduction, Devarda's alloy), 6·0. $2AgNO_3,5HCN$ requires Ag, 45·4; N, 14·8; N as NO_3, 5·9%].

Action of Mercuric Chloride on Iminoformylcarbylamine.—Addition of mercuric chloride (4 g.; 1·5 mols.) in pure dry ether (250 c.c.) to iminoformylcarbylamine (0·54 g.; 1 mol.) in pure dry ether (50 c.c.) yielded a white crystalline solid (1·24 g.), which was washed with dry ether and dried in a vacuum over sulphuric acid (Found: Hg, 56·6; N, 11·7; Cl, 19·4. $HgCl_2,3HCN$ requires Hg, 56·8; N, 11·9; Cl, 20·1%). A repetition of the experiment, but with an excess of iminoformylcarbylamine ($[HCN]_2$, 0·95 g., 2 mols.; $HgCl_2$, 2·44 g., 1 mol.), yielded the same *compound* (1·8 g.) (Found: Hg, 56·7; N, 11·8; Cl, 19·7%). The compound is somewhat soluble in dry ether and in dry benzene and very soluble in cold water.

Action of Hydrogen Chloride on the Compound $HgCl_2,3HCN$.—A solution of the compound (2 g.) in dry ether (300 c.c.) was saturated with dry hydrogen chloride. Owing to the extremely deliquescent nature of the white solid deposited, its removal, the washing with dry ether, drying, and transference to a weighing bottle for analysis were performed in a specially designed box [Found: Hg, 48·0; N, 10·0; Cl, 30·0. $2HgCl_2,3(2HCN,HCl)$ requires Hg, 49·2; N, 10·3; Cl, 30·5%].

Action of Aluminium Chloride on Iminoformylcarbylamine.—Powdered aluminium chloride (3·3 g.; 1 mol.), mixed with iminoformylcarbylamine (1·7 g.; 1·25 mols.), was heated to 85°. Liquefaction first occurred and the liquid then rapidly solidified. The solid was rapidly crushed and placed in a vacuum desiccator to remove excess of the volatile iminoformylcarbylamine. The white solid obtained had m. p. 125°, unchanged by admixture with the compound $AlCl_3,2HCN$ prepared from aluminium chloride and hydrogen cyanide (Found: Cl, 56·2; N, 14·3. Calc. for $AlCl_3,2HCN$: Cl, 56·8; N, 14·5%).

The compound was heated at 100° for 3 hours under a water-cooled condenser attached to a U-tube immersed in solid carbon dioxide and alcohol. Hydrogen cyanide condensed as a solid in the U-tube, but no iminoformylcarbylamine was detected. A similar result was obtained when the compound was heated with quinoline.

Action of Aluminium Chloride on Chloromethyleneformamidine.—When powdered aluminium chloride (7 g.; 1·16 mols.) was added to chloromethyleneformamidine (4 g.; 1 mol.), the mixture partly liquefied with evolution of heat. The liquid was decanted from unchanged aluminium chloride and allowed to cool in the absence of moisture; it then yielded a white solid, m. p. 80° (Found: Cl, 62·9; N, 12·3. $AlCl_3,2HCN,HCl$ requires Cl, 63·4; N, 12·5%).

The compound $AlCl_3,2HCN,HCl$ was maintained at 100° for 2 hours in a flask attached to a horizontal air condenser fitted with a calcium chloride tube. Chloromethyleneformamidine condensed as a volatile and very deliquescent solid in the cooler parts of the condenser and was identified by analysis and by its reaction with toluene and aluminium chloride to yield *p*-tolualdehyde (see below).

Reaction of the Compound $AlCl_3,2HCN,HCl$ *with Toluene.*—The compound (3·7 g.; 1 mol.), suspended in dry toluene (30 c.c.), was heated with aluminium chloride (2·3 g.; 1 mol.) for 1 hour on a steam-bath. The red liquid obtained was poured on ice and concentrated hydrochloric acid and distilled with steam. Phenylhydrazine (5 c.c.) was added to the distillate, which was again distilled with steam to remove toluene and the excess of phenylhydrazine, leaving *p*-tolualdehydephenylhydrazone as a yellow solid, m. p. and mixed m. p. 114° (3·2 g.; 91%, calculated on the basis that $AlCl_3,2HCN,HCl$ yields 1 mol. of aldehyde).

Action of Hydrogen Chloride on $AlCl_3,2HCN$.—Hydrogen chloride was passed over the compound (5 g., prepared from hydrogen cyanide) in a U-tube. Reaction began at 80°, the solid gradually liquefying. The passage of hydrogen chloride was then discontinued, and the contents of the tube were protected from moisture while the temperature of the bath was raised to 100°. The compound gradually dissociated and after 2 hours chloromethyleneformamidine collected on the cooler parts of the tube and was identified by the addition of toluene (30 c.c.) and aluminium chloride (3·5 g.; 1 mol.) and proceeding as described above, *p*-tolualdehydephenylhydrazone being obtained (2·8 g.; 50%, calc. on the above basis).

Action of Aluminium Chloride on the Sesquichloride of Hydrogen Cyanide.—A mixture of aluminium chloride (13·3 g.; 1 mol.) and the sesquichloride (16 g.; 1 mol.), protected from moisture, liquefied when warmed to 65°, and set to a colourless crystalline solid, m. p. 62°, on cooling (Found: Cl, 71·6; N, 9·5. $AlCl_3,2HCN,3HCl$ requires Cl, 71·7; N, 9·4%).

Excess of aluminium chloride (8 g.; 1·2 mols.), added similarly to powdered sesquichloride (8·1 g.; 1 mol.), yielded a liquid together with some unchanged aluminium chloride. Decantation and cooling of the liquid again yielded the above compound, m. p. 62°.

Reaction of the Compound $AlCl_3,2HCN,3HCl$ *with Toluene.*—The compound (37 g.; 1 mol.) in dry toluene (50 c.c.) was heated under reflux at 70° for 1 hour and at 100° for 2 hours, the evolution of hydrogen chloride then having ceased. The mixture was poured on ice and concentrated hydrochloric acid and steam-distilled. The *p*-tolualdehyde present in the distillate was determined as its phenylhydrazone by the procedure described above. In order to determine the tolylhydrylamine, the residue remaining after the initial steam distillation in acid solution was basified and again steam-distilled, the tolylhydrylamine, m. p. 92° (acetyl derivative, m. p. 157°; compare Gattermann and Schnitzpahn, *loc. cit.*), being isolated from the distillate by extraction with ether (Yields: *p*-tolualdehydephenylhydrazone, 3·6 g., 14%; tolylhydrylamine, 3·6 g., 14%).

Reaction of the Compound $AlCl_3,2HCN,3HCl$ *with Toluene in Presence of Aluminium Chloride.*—A mixture of the compound (37 g.; 1 mol.), dry toluene (43 c.c.), and aluminium chloride (17 g.; 1 mol.) was maintained under reflux at 50—55° for 3 hours; hydrogen chloride evolution being then complete, the reaction mixture was treated as described above. No phenylhydrazone was obtained from the first distillate, and the residue yielded tolylhydrylamine (22 g.; 84%).

Reaction of Iminoformylcarbylamine with Primary Aromatic Amines.—Solutions of iminoformylcarbylamine (1 mol.) and of the aromatic amine (2 mols.) in dry benzene were heated under reflux on the water-bath for a short time until the evolution of ammonia was complete and, after removal of the benzene, the solid product was purified by crystallisation. The product obtained with each amine was identical with that described by Dains (*loc. cit.*) and the yield was almost quantitative. Aniline, *p*-toluidine, *p*-bromoaniline, *p*-chloroaniline, *p*-anisidine, α- and β-naphthylamines readily yielded condensation products, but no condensation occurred with *o*- and *p*-nitroanilines, *m*-nitro-*p*-toluidine, or *p*-aminophenol (compare *idem, ibid.*).

Action of Monomethylaniline on Chloromethyleneformamidine.—Monomethylaniline (5 c.c.; 3 mols., *i.e.*, 1 mol. excess) and chloromethyleneformamidine (1·3 g.; 1 mol.) were mixed and heated at 100° for 5 minutes. The latter substance dissolved and the solution rapidly deposited a mass of fine, white, needle-shaped crystals, which were washed with dry ether, yielding *phenylmethylformamidine hydrochloride*, m. p. 192° (Found: Cl, 20·9; N, 16·3. $C_8H_{11}N_2Cl$ requires Cl, 20·8; N, 16·4%) (2·1 g.; 86%). Attempted crystallisation from alcohol or aqueous alcohol led to partial decomposition of the compound.

Action of Water on Phenylmethylformamidine Hydrochloride.—The hydrochloride (5 g.), when boiled with water (30 c.c.), yielded an oil, which was extracted with ether. The dried extract yielded, on fractionation, formomethylanilide as a light brown oil, m. p. 8—10°, b. p. 244—245° (Pinner, *Ber.*, 1883, **16**, 1652, records b. p. 243—244°) (Found: N, 10·3. Calc.: N, 10·4%) (2 g.; 50%).

Action of Sodium Hydroxide Solution on Phenylmethylformamidine Hydrochloride.—The hydrochloride (1 g.), on boiling with 4*N*-sodium hydroxide for 5 minutes, yielded monomethylaniline (0·5 g.), which was extracted in ether and identified as its hydrochloride, m. p. and mixed m. p. 121°.

Action of Monomethylaniline on the Sesquichloride.—Monomethylaniline (7 c.c.; excess over 3 mols.) was slowly added to the sesquichloride (3 g.; 1 mol.); a vigorous action ensued, and the mixture was then heated at 100° for 10 minutes. The solid product, warmed with 4*N*-hydrochloric acid, yielded formomethylanilide (4 g.), b. p. 243—245°, which was extracted with ether (Found: N, 10·3. Calc.: N, 10·4%).

Reaction of Chloromethyleneformamidine with Ethyl Alcohol.—Ethyl alcohol, distilled from sodium (26 c.c.; 4 mols.) was added to chloromethyleneformamidine (10 g.; 1 mol.), protected from moisture. On cooling by immersion in cold water for 20 hours with occasional shaking, the solid gradually dissolved, finally yielding a viscous liquid and ammonium chloride (0·6 g.) (Found: N, 26·0. Calc.: N, 26·2%). The liquid, on fractionation, yielded ethyl orthoformate, b. p. 144—145° (9·9 g.; 60·5%), and an oily residue of formamidine hydrochloride, which solidified on cooling and crystallised from alcohol in long colourless needles (8·5 g.), m. p. 81° (Found: N, 34·7. Calc.: N, 34·8%).

A repetition of the above procedure, with subsequent heating under reflux on a steam-bath for 1 hour, yielded similarly ammonium chloride (1 g.), ethyl orthoformate (10 g.; 61%), and formamidine hydrochloride (8 g.; 89%).

The reactants in molecular proportion were kept at room temperature for 20 hours and heated at 100° for 1 hour, and unchanged chloromethyleneformamidine was removed by filtration of the hot liquid, which, on cooling, deposited formamidine hydrochloride (25%) and yielded, on fractionation, ethyl orthoformate (27%).

Action of Hydrogen Chloride on Iminoformylcarbylamine in Alcoholic Solution—Dry hydrogen chloride was passed into a solution of iminoformylcarbylamine (2·16 g.; 1 mol.) in alcohol, distilled from sodium (7·4 g.; 4 mols.), protected from moisture, for 2 hours at 0°. The resulting solution was kept at room temperature for 12 hours and heated under reflux on a steam-bath for 1 hour. By the procedure described above, formamidine hydrochloride (2·5 g.; 80%) and ethyl orthoformate (4 g.; 68%) were isolated.

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