

CCXXXVII.—*Studies on Hydrogen Cyanide. Part II.*
The Compounds formed by the Action of the
Hydrogen Halides on Hydrogen Cyanide.

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THE first reference to the behaviour of hydrogen cyanide towards the halogen acids is by Gal and Gautier who, although working independently, published their results jointly (*Annalen*, 1866, **138**, 36). Gal found that whereas hydrogen bromide and hydrogen iodide were rapidly absorbed by hydrogen cyanide, giving white crystalline solids to which he assigned the formulæ HCN, HBr and HCN, HI respectively, hydrogen chloride was only slightly absorbed and no combination occurred, prolonged passage of the gas, even at -10° , completely volatilising the hydrogen cyanide.

Gautier (*Ann. Chim. Phys.*, 1869, **17**, 105) saturated anhydrous hydrogen cyanide with hydrogen chloride at -15° , and by alternately heating the mixture to $35-40^\circ$ under pressure and cooling it, obtained a crystalline substance corresponding to the formula HCN, HCl . He concluded that no reaction occurred unless the mixture was heated under pressure, since distillation of the mixture gave unchanged reagents.

Claisen and Matthews (*Ber.*, 1883, **16**, 3088; *J.*, 1882, **41**, 264)

absorbed hydrogen chloride in a well-cooled solution of hydrogen cyanide in ethyl formate, and obtained a white crystalline hygroscopic solid corresponding to the formula $2\text{HCN}, 3\text{HCl}$, which they termed a "sesquichloride." Although the constitution of this compound has been conclusively established as $\text{CHCl}_2 \cdot \text{NH} \cdot \text{CH} \cdot \text{NH}, \text{HCl}$ by Gattermann and Schnitzspahn (*Ber.*, 1898, **31**, 1770) and has been corroborated by Dains (*Ber.*, 1902, **35**, 2496), the existence of Gautier's compound has never been substantiated. Claisen and Matthews (*loc. cit.*) suggest the possibility of their compound being identical with that of Gautier, whereas Nef (*Annalen*, 1895, **287**, 320) regards the latter as being $2\text{HCN}, 2\text{HCl}$ and considers it and the sesquichloride to be additive compounds of hydrogen chloride and iminoformyl cyanide ($\text{NH} \cdot \text{CH} \cdot \text{CN}$).

In the recorded properties of these two compounds noticeable differences occur. Gattermann and Schnitzspahn note that the sesquichloride is not very hygroscopic, whereas Gautier describes his compound as being extremely so. The sesquichloride melts at 180° (decomp.) (Claisen and Matthews, *loc. cit.*), whereas Gautier's compound becomes yellow when heated above 100° , and if quickly heated, partially melts and sublimes. Such differences are not unexpected in view of the big variation in the conditions under which the two compounds were formed. It was therefore considered essential to make a more detailed study of the properties of the sesquichloride.

When the sesquichloride (prepared according to the method of Claisen and Matthews) is kept over solid sodium hydroxide in a vacuum desiccator it gradually loses hydrogen chloride until, after several months, its chlorine content drops from 66.1 to 40%, a value below that required for Gautier's compound, *i.e.*, 55.9%. A similar but much more rapid decomposition also occurs when the sesquichloride is heated to 100° , the volatile solid obtained having Cl, 39.2%, which corresponds to $2\text{HCN}, \text{HCl}$. This decomposition affords an explanation of the difference between Gautier's and Claisen and Matthews's results. Under the conditions employed by the former there must always be some decomposition of the sesquichloride, and it would seem that his compound was probably a mixture of the sesquichloride, $2\text{HCN}, 3\text{HCl}$, and its decomposition product, $2\text{HCN}, \text{HCl}$. Several repetitions of Gautier's experiment yielded white solids which had no definite composition, the chlorine contents varying between 59 and 65%. The compound $2\text{HCN}, \text{HCl}$ can also be readily obtained from the sesquichloride by heating the latter with excess of liquid hydrogen cyanide—this is essentially a feature of Gautier's experiments since he never had an excess of hydrogen chloride.

Although hydrogen chloride dissolves in hydrogen cyanide without any apparent action at low temperatures, and the mixture can be separated by distillation, nevertheless if the passage of the former be maintained for about an hour, combination occurs without the aid of any external heating, the crystals so deposited being pure sesquichloride. A similar latent period was also observed when the reaction was carried out in the presence of solvents such as ether, nitrobenzene, and esters.

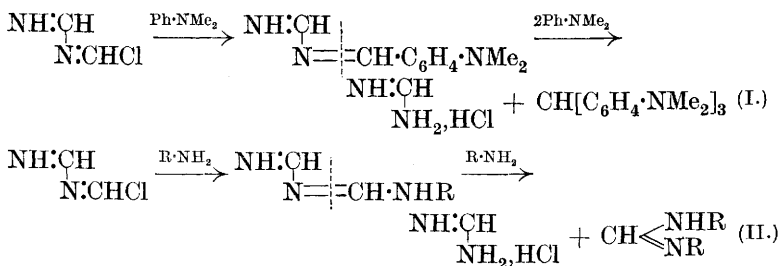
The compound $2\text{HCN}\cdot\text{HCl}$ has now been proved to be *chloromethyleneformamidine*, $\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{CHCl}$. When it is heated with quinoline, hydrogen chloride is eliminated, producing an almost quantitative yield of bimolecular hydrogen cyanide, the so-called iminoformyl cyanide of Nef, who obtained it only in exceedingly small quantity by heating the sesquichloride with quinoline. According to Willstätter and Wirth (*Ber.*, 1909, **42**, 1908), this compound is also produced to a small extent when thioformamide is heated under reduced pressure.

Bimolecular hydrogen cyanide, from its relationship to the sesquichloride, should be iminoformyl *isocyanide*, $\text{NH}\cdot\text{CH}\cdot\text{NC}$. The presence of the *isocyanide* group has been proved by the reaction of the compound with phenyl magnesium iodide, in which the *isonitrile* group is eliminated as benzaldehyde according to the scheme: $\text{NH}\cdot\text{CH}\cdot\text{NC} + \text{Ph}\cdot\text{Mg}\cdot\text{Br} \longrightarrow \text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{C} \begin{smallmatrix} \text{Ph} \\ \text{MgBr} \end{smallmatrix} \xrightarrow{\text{H}_2\text{O}} \text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{C} \begin{smallmatrix} \text{Ph} \\ \text{H} \end{smallmatrix} \xrightarrow{\text{H}_2\text{O}} \text{Ph}\cdot\text{CHO} + \text{H}\cdot\text{CO}_2\text{H} + 2\text{NH}_3$.

Further evidence for the *isocyanide* structure of bimolecular hydrogen cyanide is supplied by its behaviour with hydrogen chloride: it readily combines with only one mol. to form chloromethyleneformamidine, and not the sesquichloride as claimed by Nef: $\text{NH}\cdot\text{CH}\cdot\text{NC} + \text{HCl} \longrightarrow \text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{CHCl}$. Chloromethyleneformamidine reacts with benzene in presence of aluminium chloride, giving benzaldehyde as final product, and this can only occur if the chlorine atom is directly attached to the carbon atom of the *isocyanide* radical: $\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{CHCl} + \text{C}_6\text{H}_6 \longrightarrow$



This reaction emphasises the similarity of structure between chloromethyleneformamidine and the sesquichloride (compare Gattermann and Schnitzspahn, *loc. cit.*), which is further substantiated by the behaviour of these two compounds with dimethylaniline and with aniline. With the former they both yield hexamethyltriaminotriphenylmethane (I) and with the latter they yield diphenylformamidine (II) (compare Dains, *loc. cit.*). The cleavages must occur in a similar manner in each compound:



Hydrogen bromide is rapidly absorbed by well-cooled hydrogen cyanide and after a very short latent period the liquid is rapidly transformed into a white solid mass of the *sesquibromide*, $2\text{HCN}, 3\text{HBr}$. Contrary to the observations of Gal and Gautier (*loc. cit.*), hydrogen iodide combines rapidly with hydrogen cyanide, giving rise to the *sesqui-iodide* $2\text{HCN}, 3\text{HI}$, and not the monoiodide HCN, HI . The difference in the readiness with which the three hydrogen halides react with hydrogen cyanide is in accordance with their recognised variation in stability with increasing atomic volume of the halogen (compare Kossel, *Ann. Physik*, 1916, **49**, 270).

The *sesquibromide* and *sesqui-iodide* are very similar to the *sesquichloride* and readily evolve the hydrogen halide when heated, probably forming the hydrogen halide of bimolecular hydrogen cyanide, $2\text{HCN}, \text{HX}$. The hydrobromide of the latter compound is also formed by the action of hydrogen bromide upon bimolecular hydrogen cyanide and is a white solid more hygroscopic than the corresponding hydrochloride.

EXPERIMENTAL.

The hydrogen cyanide used in this investigation was prepared by the method described by Coates, Hinkel, and Angel (*J.*, 1928, 542). The *sesquichloride* was prepared by saturating a well-cooled solution of hydrogen cyanide in anhydrous ether with hydrogen chloride. The crystals which formed were rapidly drained, washed with ether, and quickly transferred to a desiccator.

The Action of Heat on the Sesquichloride.—The *sesquichloride* was heated in a round-bottomed flask connected to a horizontal glass tube which served as an air-condenser. The flask was immersed in a steam-bath and the apparatus connected to a water-pump. A quantity of liquid and a small amount of solid collected in the tube. On cooling, the liquid solidified to a transparent glass-like mass of *chloromethyleneformamidine*, which contracted and assumed a cracked appearance (Found: Cl, 40.9; N, 29.5. $2\text{HCN}, \text{HCl}$ requires Cl, 39.2; N, 30.9%). The discrepancies in

the analyses are possibly due to the occlusion of free hydrogen chloride in the solid during solidification. The light brown residue in the flask could not be purified, but appeared to have a similar composition although contaminated with azulmin products (Found : Cl, 36.8; N, 28.5%).

The Reaction of Chloromethyleneformamidine with Benzene and Aluminium Chloride.—The chloro-compound (2.5 g.) was suspended in dry benzene (20 g.), and powdered aluminium chloride (6.5 g.) added. When the vigorous action, which only occurred on warming, had subsided, the resulting dark solution was poured on a mixture of ice and concentrated hydrochloric acid, and distilled in steam. Phenylhydrazine (5 c.c.) was then added to the distillate, and the mixture distilled in steam to remove benzene and excess of phenylhydrazine. The yellow solid remaining in the flask had m. p. 157°, unchanged when admixed with benzaldehydephenylhydrazone.

The Action of Hydrogen Cyanide on the Sesquichloride, 2HCN, 3HCl.—A small quantity of the pure sesquichloride was heated with liquid hydrogen cyanide in a sealed glass tube for several days at 40°. The excess of hydrogen cyanide was then rapidly removed under reduced pressure. The white solid residue contained Cl, 44%, and yielded benzaldehydephenylhydrazone when treated with benzene and aluminium chloride as described above.

Formation of Hexamethyltriaminotriphenylmethane (Crystal Violet Leuco-base) from Chloromethyleneformamidine.—The chloro-compound (3.5 g.) was mixed with dimethylaniline (15 c.c.) and heated to 100°; the product consisted of a deep violet layer below unchanged dimethylaniline. The warm mass was made alkaline with caustic soda and distilled in steam. The solid residue was washed with small quantities of alcohol to remove the dark colouring matter, and dissolved in a mixture of benzene and light petroleum (b. p. 40–60°), from which it separated in colourless prismatic needles, m. p. 177° (Found : N, 11.3. Calc. for $C_{25}H_{31}N_3$: N, 11.3%).

Formation of Diphenylformamidine.—Aniline (2.6 c.c.; 2 mols.) was added drop by drop to chloromethyleneformamidine (1 g.; 1 mol.); a vigorous reaction took place, and the resulting solid crystallised from alcohol as needles, m. p. 142° (Found : N, 14.1. Calc. for $C_{13}H_{12}N_2$: N, 14.3%).

Bimolecular Hydrogen Cyanide (Iminoformyl isoCyanide).—When the sesquichloride (1 mol.) is heated with slightly more than 3 mols. of quinoline, bimolecular hydrogen cyanide is produced in about 60% yield; the reaction is, however, very vigorous and difficult to regulate, and it is probably on this account and owing to the extreme volatility of the product that Nef (*loc. cit.*) obtained it

only in extremely small yields. It can be readily prepared almost quantitatively by gently heating chloromethyleneformamidine (1 mol.) with quinoline (1 mol.) and passing the vapours by means of a stream of air through a U-tube cooled with solid carbon dioxide, whereupon it is deposited as a white solid, m. p. 85° .

Preparation of Chloro- and Bromo-methyleneformamidines from Bimolecular Hydrogen Cyanide.—Ethereal solutions of bimolecular hydrogen cyanide were saturated with hydrogen chloride and bromide respectively, a white solid being precipitated in each case. The ether and excess of hydrogen halide were rapidly removed under reduced pressure, and the resulting solids analysed (Found: Cl, 38.4. $2\text{HCN}, \text{HCl}$ requires Cl, 39.2%. Found: Br, 55.0. $2\text{HCN}, \text{HBr}$ requires Br, 59.2%). The low bromine result is due to the very hygroscopic nature of the compound.

The Formation of Benzaldehyde from Bimolecular Hydrogen Cyanide.—Phenyl magnesium bromide, prepared by dissolving magnesium (1.33 g.) in a solution of bromobenzene (8.7 g.) in ether (25 c.c.), was slowly added to bimolecular hydrogen cyanide (3 g.) in ether (20 c.c.). A vigorous reaction occurred and a white solid was formed. After 1 hour's heating, the mixture was poured on ice and hydrochloric acid, and distilled in steam. The benzaldehyde was isolated in the distillate as its phenylhydrazone, m. p. 157° , as described on p. 1838.

Preparation of Sesquibromide and Sesqui-iodide of Hydrogen Cyanide.—The dry hydrogen halide was passed into anhydrous hydrogen cyanide cooled to -10° . In each case separation of a white solid began almost immediately and a semi-solid mass was finally obtained. The solids were washed with dry ether and dried in a vacuum. The *sesquibromide* partially sublimes on heating and melts with decomposition at 240° (Found: Br, 82.6. $2\text{HCN}, 3\text{HBr}$ requires Br, 80.6%). The *sesqui-iodide* darkens on heating and melts with decomposition at $158-160^{\circ}$ (Found: I, 90.9. $2\text{HCN}, 3\text{HI}$ requires I, 87.0%).

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