37. *Studies on Hydrogen Cyanide. Part VI. The Mechanism of Gattermann's Hydrogen Cyanide Aldehyde Synthesis.*

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In the synthesis of aromatic aldehydes from phenols and phenolic ethers by means of hydrogen cyanide and hydrogen chloride in presence of aluminium chloride, Gattermann and his co-workers (*Ber.*, 1898, **31**, 1149, 1766; 1899, **32**, 278; *Annalen*, 1909, **357**, 313) considered that the primary product is iminoformyl chloride, NH:CHCl, whereas Hinkel, Ayling, and Morgan (J., 1932, 2793) regarded it as chloromethyleneformamidine, NH:CH·N:CHCl.

A valuable insight into the mechanism of the reaction is afforded by the observation (Hinkel, Ayling, and Beynon, J., 1935, 674) that the compound $AlCl_3,2HCN$ unites with hydrogen chloride at 80°, forming $AlCl_3,2HCN,HCl$, identical with the product obtained by the direct union of chloromethyleneformamidine with aluminium chloride. This double compound dissociates on heating into chloromethyleneformamidine, which in presence of free aluminium chloride reacts readily with hydrocarbons and phenolic ethers, giving arylmethyleneformamidine hydrochlorides; these on hydrolysis yield the aldehydes. It is therefore not necessary to postulate the dissociation of the double compound $AlCl_3,2HCN$ in the Gattermann synthesis as originally suggested (Hinkel, Ayling, and Morgan, *loc. cit.*), since it appears that hydrogen cyanide in the presence of aluminium chloride always reacts as the dimeride, giving derivatives of iminoformylcarbylamine, NH:CH·NC.

On the other hand, in the absence of aluminium chloride, a solution of hydrogen chloride in hydrogen cyanide consists potentially of iminoformyl chloride, although distillation leads to the recovery of the hydrogen cyanide, and the only compound isolated is the sesquichloride, dichloromethylformamidine hydrochloride (compare Hinkel and Dunn, J., 1930, 1836). Therefore, when hydrogen cyanide and hydrogen chloride react with resorcinol in ethereal solution (Gattermann and Köbner, *Ber.*, 1899, **32**, 278) or with ethyl alcohol (Pinner, *Ber.*, 1883, **16**, 352), the resulting hydrochloride of resorcylaldimine or of iminoformyl ethyl ether, respectively, must owe its formation to the presence of iminoformyl chloride. These reactions definitely confirm the primary reaction as the tendency to form iminoformyl chloride before derivatives of the dimeride, iminoformylcarbylamine, since the latter, when treated in a similar manner, yields formamidine hydrochloride and ethyl orthoformate (Hinkel, Ayling, and Beynon, *loc. cit.*).

When hydrogen cyanide is replaced by iminoformylcarbylamine in the resorcylaldehyde synthesis, a somewhat similar reaction occurs. In place of the white or pink-tinged resorcylaldimine hydrochloride, however, yellow *resorcylmethyleneformamidine hydrochloride*, $C_6H_3(OH)_2·CH:N·CH:NH,HCl$, separates, and this, on hydrolysis, also yields resorcylaldehyde. The primary reaction in this case is the formation of chloromethyleneformamidine, which then reacts directly with resorcinol. The yellow compound so formed is not decomposed into the aldimine hydrochloride by excess of hydrogen chloride or resorcinol.

In the similar action with hydrogen cyanide, the presence of the formamidine derivative has not been detected and no derivative of iminoformylcarbylamine results unless the temperature is kept at 0° throughout. Under the latter condition, the reaction between the iminoformyl chloride and resorcinol is depressed so that part of the hydrogen cyanide appears as the " sesquichloride," admixed with the resorcylaldimine hydrochloride.

The exact mode of formation of the sesquichloride from hydrogen cyanide and hydrogen chloride is still not clear, but the initial stage must be the formation of iminoformyl chloride, which only exists potentially, similarly to formyl chloride. In the absence of any reactive substance, such as resorcinol or alcohol, the molecules of iminoformyl chloride combine to form chloromethyleneformamidine: $NH{:}CHCl + NH{:}CHCl \longrightarrow NH{:}CH{\cdot}N{:}CHCl$. Since, however, the latter does not yield the sesquichloride with hydrogen chloride (Hinkel and Dunn, *loc. cit.*), it is probable that, only during the moment of union of the molecules of iminoformyl chloride, at the low temperature, can the further combination with hydrogen chloride occur.

EXPERIMENTAL.

Action of Hydrogen Cyanide and Hydrogen Chloride upon Resorcinol in Ether.—(i) *At room temperature.* When an experiment was carried out under the conditions used by Gattermann and Kōbner (*Ber.*, 1899, **32**, 278), the yield of resorcylaldehyde (calculated on the resorcinol taken) was 58%, in close agreement with that obtained by Hinkel, Ayling, and Morgan (J., 1932, 2793). Dilution of the decanted ether with an equal volume of dry ether caused a further precipitation of the aldimine hydrochloride, m. p. 166° (decomp.), thereby giving a total yield of resorcylaldehyde of 72%.

(ii) *At* 0°. When the above experiment was repeated at 0°, the crystalline solid obtained, m. p. 166—170° (decomp.) (Found: N, 10·0; Cl, 31·7%), corresponded to a mixture of the aldimine hydrochloride (Calc.: N, 8·1; Cl, 20·5%) and the sesquichloride (Calc.: N, 17·1; Cl, 65·1%). Hydrolysis of the solid yielded resorcylaldehyde (56%, calculated on the resorcinol used).

An almost complete conversion of the resorcinol into the aldehyde can be obtained only when the hydrogen cyanide is in excess and the experiment is carried out at laboratory temperature, and even then the aldimine hydrochloride first precipitated is always contaminated with some sesquichloride.

Other solvents, such as tetrachloroethane, *o*-dichlorobenzene, chlorobenzene, and benzene, can replace the ether in the preparation.

Action of Iminoformylcarbylamine and Hydrogen Chloride upon Resorcinol.—When dry hydrogen chloride was slowly passed into a solution of iminoformylcarbylamine (Hinkel, Ayling, and Beynon, *loc. cit.*) (1 g.; 1 mol.) and resorcinol (2·6 g.; 1·2 mols.) in dry ether (100 c.c.) under a reflux condenser at room temperature with exclusion of moisture, a bright yellow powder began to be deposited after 15 minutes. It was collected after 3 hours, washed with ether (40 c.c.), and dried in a vacuum, yielding *resorcylmethyleneformamidine hydrochloride*, m. p. 135° (decomp.) (Found: N, 14·0; Cl, 17·8. $C_8H_9O_2N_2Cl$ requires N, 14·0; Cl, 17·7%). Yield, 3·6 g. (97%, calculated on the iminoformylcarbylamine). The yellow compound (2·5 g.), when boiled for 5 minutes with water (10 c.c.) and 4*N*-hydrochloric acid (1 c.c.), yielded resorcylaldehyde (1·6 g.; 93%) as golden-yellow needles, m. p. and mixed m. p. 135°.

Action of Chloromethyleneformamidine upon Resorcinol.—Resorcinol (2·4 g.; 1 mol.) was shaken for 12 hours with a suspension of finely powdered chloromethyleneformamidine (Hinkel, Ayling, and Beynon, *loc. cit.*) (2 g.; 1 mol.) in dry ether (20 c.c.) in a sealed flask at room temperature. The yellow powder obtained, after being washed with ether (20 c.c.) and dried in a vacuum, yielded resorcylmethyleneformamidine hydrochloride (4 g.; 90%), m. p. 135° (decomp.). Hydrolysis of the compound (2 g.) with dilute acid as above yielded resorcylaldehyde (1·2 g.; 87%).

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