

### 342. Studies on Hydrogen Cyanide. Part XVII. The Alleged Resorcylaldimine Hydrochloride.

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The reaction between resorcinol and hydrogen cyanide in presence of hydrogen chloride has been investigated and it has been shown that the alleged aldimine hydrochloride is probably a derivative of the sesquichloride of hydrogen cyanide containing two molecules of resorcinol, one of which is attached through the nucleus whilst the other is attached as an *O*-ether.

A dialdimine hydrochloride has been prepared which differs from the above compound in having both molecules of resorcinol attached through the nucleus.

The view is expressed that, in order to account for their salt-forming properties, formylimino ethers may also be derivatives of the sesquichloride of hydrogen cyanide.

WHEREAS Gattermann and his co-workers (*Ber.*, 1898, **31**, 1766; 1899, **32**, 278; *Annalen*, 1909, **357**, 313) considered the primary product in the hydrogen cyanide synthesis of aromatic aldehydes to be iminoformyl chloride  $\text{NH}\cdot\text{CHCl}$ , Hinkel, Ayling, and Morgan (*J.*, 1932, **2793**) regarded it as chloromethyleneformamidine  $\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{CHCl}$  and suggested that the resorcylaldimine hydrochloride of Gattermann was resorcylmethyleneformamidine hydrochloride  $(\text{OH})_2\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{N}\cdot\text{CH}\cdot\text{NH}\cdot\text{HCl}$ . Subsequently, however, Hinkel, Ayling, and Beynon (*J.*, 1936, 184) obtained the latter compound, as a bright yellow substance, by interaction of chloromethyleneformamidine with resorcinol.

Since the resorcylaldimine hydrochloride of Gattermann is almost white, it cannot have the structure suggested by Hinkel, Ayling, and Morgan (*loc. cit.*).

Although the yields of resorcylaldehyde obtained under Gattermann's conditions are invariably about 50% calculated on the resorcinol, yet the supernatant ether contains only a very small amount of dissolved solid. Almost the whole of the resorcinol must therefore have been used in the reaction, yielding a compound from which only a part of the original resorcinol is recoverable as resorcylaldehyde on hydrolysis.

It has now been found that this compound always yields on hydrolysis a mixture of resorcylaldehyde and resorcinol together with formic acid and ethyl ether.

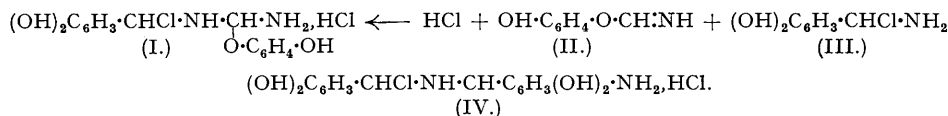
It is probable therefore that part of the resorcinol is united in the molecule as a phenolic ether. Houben (*Ber.*, 1926, **59**, 2878) has shown that phenols can react with hydrogen cyanide and hydrogen chloride to yield iminomethyl ethers  $\text{NH}\cdot\text{CH}\cdot\text{OR}$  which are readily hydrolysed to regenerate the phenols.

The product settles out in the first instance as a thick liquid which becomes semi-solid overnight. If the supernatant ethereal solution be decanted and the thick liquid or semi-solid kept in a desiccator, the syrup becomes hard and brittle. It is significant that the product obtained in several repetitions under Gattermann's conditions, whether liquid, semi-solid, or hard, always gave the same analytical results for nitrogen and chlorine. The yield of resorcylaldehyde does vary slightly, depending on the initial temperature and on the rate at which the hydrogen chloride is passed into the reaction mixture. Thus it is possible (see Experimental) under suitable conditions, particularly at low temperature, to obtain a product in which all the combined resorcinol is recoverable as resorcylaldehyde. It is therefore highly probable that Gattermann's product is not the true aldimine hydrochloride (IV) but a derivative of the sesquichloride of hydrogen cyanide  $\text{CHCl}_2\cdot\text{NH}\cdot\text{CHCl}\cdot\text{NH}_2$  having the structure (I) in combination with one molecule of ethyl ether. The compound may have associated with it varying quantities of the true aldimine hydrochloride (IV) also in combination with one molecule of ethyl ether, so that, whilst the yield of resorcylaldehyde may vary, the analytical percentages of nitrogen and chlorine remain unchanged. Furthermore, the product when kept *in vacuo* slowly loses the combined ethyl ether yielding a solid which, from its nitrogen and chlorine contents, corresponds to (I) or (IV).

The suggested structure accounts for the formation of resorcylaldehyde, resorcinol, and formic acid on hydrolysis. Its formation can be explained through the intermediates iminoformyl chloride ( $\text{CHCl}\cdot\text{NH}$ ) and formamidodichloride [dichloromethylamine],  $\text{CHCl}_2\cdot\text{NH}_2$ ; thus the iminoformyl chloride, by reacting with resorcinol, could form an iminomethyl ether (II), whilst formamidodichloride can give rise to  $\omega$ -chloro- $\omega$ -aminomethylresorcinol (III). These two products by condensation in the presence of free hydrogen chloride could give rise to the sesquichloride derivative (I).

It has been shown (Hinkel and Watkins, *J.*, 1944, 647) that, owing to the readiness with which formamido dichloride dissociates, on dilution, into iminoformyl chloride and its

components, the yield of aldehyde under Gattermann's conditions decreases with dilution of the reactants. It is to be expected that under these conditions imino-ether formation should occur.



In Gattermann's experiments, since hydrogen chloride is being gradually added to the solution of hydrogen cyanide, there must always be some iminoformyl chloride present during the initial stages, and, since apparently it is this compound which gives rise to imino-ethers, it is hardly to be expected that the final product should be the true aldimine hydrochloride.

If this view be correct, then by altering the conditions so that the reaction mixture contains only formamidodichloride, it should be possible to inhibit the formation of imino-ethers. This expectation has now been realised.

When hydrogen cyanide is added quickly at a low temperature to a concentrated solution of resorcinol in ether containing an excess of hydrogen chloride, a solid is obtained which corresponds by analysis to the *aldimine hydrochloride* (IV), which in this case is devoid of any combined solvent ether. This compound can be more readily prepared by substituting ethyl acetate for ether as a solvent.

Although hydrogen chloride is much less soluble in ethyl acetate than in ether, yet it seems that the dissociation of formamidodichloride does not occur so readily; thus, using Gattermann's conditions and quantities, but ethyl acetate, it is possible to obtain even at room temperature the anhydrous hydrochloride free from any phenolic ether.

Since the supposed resorcyldimine hydrochloride is only slowly hydrolysed in the cold by water, it does not seem that it owes its basic properties to the C:NH group especially as in such compounds as NH:CH·NC, NH:CH·N·CHCl, NH:CH·NR<sub>2</sub>, and NH:C(CN)·CH(CN)·NH<sub>2</sub> the NH:C group does not appear to exhibit any basic properties. It would therefore seem more probable that the supposed aldimine is really a dialdimine (IV).

This view raises doubts about the generally accepted structure of the hydrochlorides of formimino ethers, RO·CH:NH·HCl. It seems more probable from their mode of preparation that these compounds also are derivatives of the sesquichloride of hydrogen cyanide or di-imino ethers, RO·CHCl·NH·CH(OR)·NH<sub>2</sub>·HCl.

#### EXPERIMENTAL.

*Reactions in Ethyl Ether.*—(a) *Addition of hydrogen chloride to hydrogen cyanide and resorcinol at room temperature.* The product obtained by slowly saturating a solution of resorcinol (8 g.; 1 mol.) and hydrogen cyanide (3 c.c.; 1 mol.) in pure dry ether (30 c.c.) with hydrogen chloride according to the directions of Gattermann and Kobner (*Ber.*, 1899, **32**, 278) was set aside overnight and the supernatant ether was then decanted. The solvated product was analysed, nitrogen being determined by distillation with alkali and chlorine by precipitation with silver nitrate. The aldehyde was determined by dissolving the compound in the least amount of water and heating for  $\frac{1}{2}$  hour on a steam-bath to remove the combined ether and to effect hydrolysis. After the mixture had cooled, resorcyldaldehyde separated as white crystals, which, after washing with a small quantity of cold water, were dried and weighed; after crystallisation from hot water it melted at 136° [Found: N, 6.5; Cl, 16.2; aldehyde, 31.9. C<sub>14</sub>H<sub>15</sub>O<sub>4</sub>N<sub>2</sub>Cl·HCl, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O requires N, 6.6; Cl, 16.8; aldehyde, 32.7%]. When the product is left in a vacuum desiccator for some weeks, it loses the combined ether yielding a hard yellowish solid [Found: N, 8.1; Cl, 20.4; aldehyde, 39.4. C<sub>14</sub>H<sub>15</sub>O<sub>4</sub>N<sub>2</sub>Cl·HCl (I) requires N, 8.0; Cl, 20.46; aldehyde, 39.8%]. The filtrate from the aldehyde was thoroughly extracted with ether. After removal of ether, the dark-coloured residue yielded, by careful sublimation, crystals of resorcinol which gave the characteristic nitroso-test with sodium nitrite in acetic acid, followed by alkali. The aqueous solution after extraction with ether yielded formic acid on distillation with dilute sulphuric acid.

A repetition of the above experiment, but at a low temperature (ice-salt), yielded a cream-coloured product as soft crystals [Found: N, 6.6; Cl, 16.8; aldehyde, 62.4. C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>NCl<sub>0.5</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O requires N, 6.6; Cl, 16.8; aldehyde, 65.5%]. These crystals, after being kept in a vacuum desiccator for many days, lose the combined ether and change into a yellow powder [Found: N, 8.1; Cl, 19.9; aldehyde, 74.9. C<sub>14</sub>H<sub>15</sub>O<sub>4</sub>N<sub>2</sub>Cl·HCl (IV) requires N, 8.0; Cl, 20.46; aldehyde, 79.5%].

In an experiment at 0° the yields of the aldehyde in the product, before and after keeping in a vacuum desiccator, were 52.8 and 64.4%, respectively. The higher values for the aldehyde in the last two experiments indicate the presence of much aldimine with the first product.

(b) *Addition of hydrogen cyanide to excess of hydrogen chloride and resorcinol.* Hydrogen chloride was passed into anhydrous ether (30 c.c.), cooled to -40° (alcohol and CO<sub>2</sub>), until the gain was 11.5 g. (1.16 mols.); resorcinol (29.8 g., 1 mol.), followed by hydrogen cyanide (9.9 c.c., 1 mol.), were then added, and the whole thoroughly mixed. The firmly stoppered \* vessel with its contents was kept at

\* If the temperature is allowed to rise, the reaction may proceed with explosive violence.

$-40^{\circ}$  for a day, whereupon a mass of cream-coloured crystals separated. The temperature of the mixture was allowed to rise to  $-25^{\circ}$ , and the supernatant ether decanted; the crystal mass was disintegrated and rapidly washed with several portions of well-cooled anhydrous ether. The crystals (*o*-chloro-*o*-aminomethylresorcinol) were rapidly dried on a porous saucer and finally for a few minutes in a vacuum desiccator (Found: N, 7.9; Cl, 19.9; aldehyde, 78.8.  $C_7H_8O_2NCl$  requires, N, 8.0; Cl, 20.46; aldehyde, 79.5%).

*Experiments in Ethyl Acetate.*—Since hydrogen chloride is not very soluble in ethyl acetate, the following experiments were carried out according to Gattermann's directions, by passing a stream of hydrogen chloride into an ethyl acetate solution of resorcinol and hydrogen cyanide, but varying the concentrations and temperatures.

(a) *Low temperature.* (i) Hydrogen chloride was passed, to saturation, into a solution of resorcinol (8 g., 1 mol.) and hydrogen cyanide (3 c.c., 1 mol.) in pure ethyl acetate (25 c.c.) cooled to  $-17^{\circ}$ , the gain in weight being 10 g. (3 mols.). The solution remained clear; after five hours at  $-17^{\circ}$  a mass of fine, almost white, solvated crystals separated. These were removed, washed with ethyl acetate, and dried *in vacuo* for two days; they then had m. p.  $95^{\circ}$  (complete at  $120^{\circ}$ ). When they were dissolved in warm water ethyl acetate was evolved (Found: N, 5.4; Cl, 12.8; aldehyde, 52.2.  $C_7H_8O_2NCl, C_4H_8O_2$  requires N, 5.3; Cl, 13.6; aldehyde, 52.8%).

(ii) Repetition of the above experiment, using 30 c.c. instead of 25 c.c. of ethyl acetate, yielded a solvate as white needles, m. p.  $140^{\circ}$  (Found: N, 6.4; Cl, 16.0; aldehyde, 63.0.  $C_7H_8O_2NCl, 0.5C_4H_8O_2$  requires N, 6.4; Cl, 16.3; aldehyde, 63.4%).

(b) *Room temperature.* (i) Hydrogen chloride was passed slowly into a solution of resorcinol (8 g., 1 mol.) and hydrogen cyanide (3 c.c., 1 mol.) in pure ethyl acetate (30 c.c.) at room temperature. The absorption of hydrogen chloride was very slow; after 1 hour a light pink precipitate was formed, the passage of the gas being continued until precipitation seemed complete. The precipitate was filtered off, washed with ethyl acetate, and dried on a porous plate; a pink powder was obtained which did not melt on heating (Found: N, 8.1; Cl, 20.5; aldehyde, 78.8. Calc. for  $C_7H_8O_2NCl$ : N, 8.07; Cl, 20.46; aldehyde, 79.5%).

(ii) With more concentrated solutions, *e.g.*, 25 c.c. of ethyl acetate, the above reaction generates considerable heat causing secondary reactions, and the product is a deep red powder.

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