220. *Studies on Hydrogen Cyanide. Part XVI. The Constitution of the "Sesquichloride."*

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The view previously expressed by Hinkel and Watkins (*J.*, 1944, 647) on the constitution of the sesquichloride of hydrogen cyanide has been supported by a study of its aluminium chloride compounds. The sesquichloride unites with two molecules of aluminium chloride yielding a product which reacts with benzene in the presence of free aluminium chloride, giving rise to a mixture of diphenylmethane, anthracene, and triphenylcarbinol with only a small amount of benzhydrylformamidine hydrochloride.

BY reaction between the sesquichloride of hydrogen cyanide and benzene in the presence of free aluminium chloride, Gattermann and Schnitzpahn (*Ber.*, 1898, **31**, 1770) obtained the hydrochloride of benzhydrylformamidine (I), and consequently assigned to the sesquichloride the structure of dichloromethylformamidine hydrochloride (II).

$CHPh_2\cdot NH\cdot CH{:}NH$ (I.) $CHCl_2\cdot NH\cdot CH{:}NH,HCl$ (II.)

Hinkel and Watkins (*loc. cit.*), in studying the action of hydrogen chloride on hydrogen cyanide, considered that the sesquichloride results as a union between formimidochloride and formamidodichloride, and therefore regarded the sesquichloride as chloro-*N*-(dichloromethyl)methylenediamine (III).

$CHCl{:}NH + CHCl_2\cdot NH_2 \longrightarrow CHCl_2\cdot NH\cdot CHCl\cdot NH_2$ (III.)

Evidence in support of this view has now been obtained through a further study of the action of aluminium chloride on the sesquichloride in the presence of benzene. Aluminium chloride readily combines with 1 mol. of the sesquichloride (Hinkel, Ayling, and Beynon, *J.*, 1935, 674), and the compound so formed reacts slowly with toluene in the presence of free aluminium chloride yielding as final product the tolylhydrylamine but only in 84% yield, whereas the uncombined sesquichloride reacts vigorously and almost quantitatively with toluene in the presence of free aluminium chloride.

The above additive compound of aluminium chloride with the sesquichloride readily unites with a further molecule of aluminium chloride on heating, and at the same time a remarkable change occurs within the molecule. The dark product does not solidify on cooling but, unlike the above mono-derivative, reacts vigorously with benzene in the presence of free aluminium chloride yielding diphenylmethane, anthracene, and triphenylcarbinol together .with only a small amount of the expected benzhydrylformamidine hydrochloride.

It would appear that the additional molecule of aluminium chloride has caused the sesquichloride molecule to undergo incipient or partial disruption into active fragments, which in the presence of free aluminium chloride unite with the benzene; thus, in the reaction mixture before hydrolysis, the characteristic odour of diphenylmethane can readily be detected. The diphenylmethane and also the anthracene, unlike the triphenylcarbinol, cannot be hydrolysis products.

The formation of anthracene and triphenylcarbinol is highly significant since these compounds indicate the presence of $\cdot NH\cdot CHCl\cdot NH_2$ in the original molecule, thus giving support to the constitution (III).

It is evident that at one stage, either before or after partial disruption, the halogens on the carbon atom must have reacted with benzene under the influence of the free aluminium chloride giving rise to the completely and the partly disrupted fragment, $CHPh{:}$ and $\cdot NH\cdot CHPh\cdot NH_2$. It is highly probable that the anthracene owes its origin to a union of 2 mols. of the benzylidene fragments. In the second case, the fragment $\cdot NH\cdot CHPh\cdot NH_2$ would probably be in combination with the aluminium chloride through one of the nitrogen atoms, and reacting further with benzene under the influence of free aluminium chloride, would yield a complex with the latter which on hydrolysis affords triphenylcarbinol.

It is not necessary to unite the sesquichloride with the 2 moles of aluminium chloride before reaction with benzene, since the same results as above can be obtained when the sesquichloride is added slowly to a large excess of powdered aluminium chloride suspended in benzene at 0°.

EXPERIMENTAL.

Preparation of $2AlCl_3,2HCN,3HCl$.—Finely-powdered aluminium chloride (67 g.; 1 mol.) and the sesquichloride of hydrogen cyanide (82 g.; 1 mol.) were intimately mixed and gently heated in a flask protected from moisture until reaction set in; the mixture soon became molten, and on cooling, a white solid mass, m. p. 62°, was obtained. To the molten mass was gradually added more finely-divided aluminium chloride (67 g.; 1 mol.), the mixture being warmed on a water-bath after each addition to aid solution and combination. After complete addition, the dark mixture was heated for a further 5 minutes, and the liquid decanted from any unchanged solid and allowed to cool in a desiccator. It did not solidify even after some hours.

Reaction of $2AlCl_3,2HCN,3HCl$ *with Benzene.*—The compound prepared above was added in small portions to benzene (300 c.c.) containing powdered aluminium chloride (33·5 g.; 0·5 mol.), mechanically stirred and cooled externally with ice. A vigorous reaction ensued after each addition, hydrogen chloride being evolved; the temperature of the mixture was maintained at 0° during the addition and for several hours afterwards. The deep red benzene solution obtained when the mixture regained room temperature was poured into a mixture of concentrated hydrochloric acid and crushed ice. The benzene layer was separated, the aqueous layer shaken with two further portions of benzene (100 c.c.), and the extracts combined.

Treatment of the benzene layer. The benzene solution was steam-distilled until no more oily drops appeared in the distillate (several hours). The aqueous distillate was extracted with benzene, and the latter separated and dried. Removal of the benzene by distillation yielded diphenylmethane (16 g.) which deposited a little anthracene (0·7 g.) on cooling; the diphenylmethane was obtained by extraction with light petroleum and repeated freezings as a white solid, m. p. 23° unchanged on admixture with an authentic specimen.

The semi-solid (44 g.) in the steam-distillation flask, which consisted of triphenylcarbinol and anthracene, was extracted with light petroleum (b. p. 40—60°), in which the anthracene is only slightly soluble. Repeated crystallisations of the soluble portion from light petroleum (b. p. 60—80°) yielded triphenylcarbinol, which was finally crystallised from aqueous alcohol, from which it separated in iridescent plates, m. p. 164·5°, unchanged on admixture with an authentic specimen.

The combined, more insoluble residues from all the light petroleum extractions, consisting of anthracene, were crystallised from benzene–light petroleum (b. p. 40—60°) and finally from benzene–alcohol. Anthracene was obtained as glittering plates with a strong blue fluorescence; m. p. and mixed m. p. with pure anthracene 216·5°.

Treatment of the aqueous layer. The aqueous layer was concentrated until aluminium chloride crystals began to separate together with a small amount of a black semi-solid. This semi-solid was collected by filtration after sufficient water had been added just to dissolve the aluminium chloride, and was then boiled with aqueous sodium hydroxide until the evolution of ammonia ceased; on cooling, a brown solid was obtained (4 g.). This was a mixture of formobenzhydrylamide and benzhydrylamine which was separated by treatment with ether, in which the former is insoluble. The formobenzhydrylamide was purified by crystallisation from alcohol and was obtained as colourless crystals, m. p. 132° (identity confirmed by mixed m. p. and comparison with an authentic specimen). The benzhydrylamine in the ether extract was acetylated with acetic anhydride after removal of the ether, and the acetobenzhydrylamide, after crystallising several times from alcohol, melted at 146° unchanged on admixture with an authentic specimen.

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