532. *Studies on Hydrogen Cyanide. Part XVIII.* The Reaction of the Sesquichloride of Hydrogen Cyanide with Mesitylene in the Presence of Aluminium Chloride.*

By L. E. Hinkel and G. H. R. Summers.

When aluminium chloride is added to the sesquichloride of hydrogen cyanide in mesitylene, the hydrochloride of *N*-dimesitylmethylformamidine $CHAr_2{\cdot}NH{\cdot}CH{=}NH$ can be isolated, whilst *N*-(dimesitylmethyl)mesitylmethylenediamine $CHAr_2{\cdot}NH{\cdot}CHAr{\cdot}NH_2$, although not isolated, must be formed since hydrolysis of the reaction product gives dimesitylmethylamine and mesitaldehyde. The production of these substances provides further proof for the constitution, $CHCl_2{\cdot}NH{\cdot}CHCl{\cdot}NH_2$ of the sesquichloride of hydrogen cyanide.

If the experimental procedure is reversed and the sesquichloride is added to the aluminium chloride, numerous compounds can be isolated, including mesitylmethylamine and dimesitylamine, which appear to be derived from fragments of the sesquichloride molecule.

The constitution of the sesquichloride of hydrogen cyanide as dichloromethylformamidine hydrochloride (I) was suggested by Gattermann and Schnitzpahn (*Ber.*, 1898, **31**, 1770). Doubts about the correctness of this constitution were first raised by Hinkel and Dunn (*J.*, 1930, 1834) who found that the sesquichloride decomposed spontaneously in a vacuum to yield free hydrogen chloride and chloromethyleneformamidine (II), and that the latter compound did not reunite with hydrogen chloride.

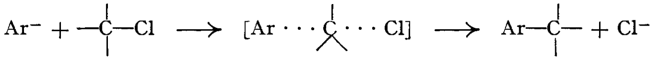
$$\underset{\text{(I)}}{CHCl_2{\cdot}NH{\cdot}CH{=}\overset{\oplus}{N}H_2\}Cl^{\ominus}} \longrightarrow \underset{\text{(II)}}{CHCl{=}N{\cdot}CH{=}NH} + HCl$$

The sesquichloride cannot be the hydrochloride of a base, as suggested by Gattermann and Schnitzpahn, because it is known that the groupings (*a*) $-CH{:}NH$ and (*b*) $CHCl_2{\cdot}NH-$ are non-basic; thus the compound $CMeCl_2{\cdot}NH_2$ is devoid of basic properties and readily loses hydrogen chloride, to give acetamidoyl chloride $CMeCl{:}NH$ (Hinkel and Treharne, *J.*, 1945, 866).

$$\underset{\text{(III)}}{CHCl{=}NH} + \underset{\text{(IV)}}{CHCl_2{\cdot}NH_2} \longrightarrow \underset{\text{(V)}}{CHCl_2{\cdot}NH{\cdot}CHCl{\cdot}NH_2}$$

Hinkel and Watkins (*J.*, 1944, 647) showed that the formation of the sesquichloride from hydrogen cyanide and hydrogen chloride results from union of the initially formed formimidoyl chloride (III) and dichloromethylamine (IV). According to these authors, the sesquichloride is correctly represented as chloro-*N*-dichloromethylmethylenediamine (V), and is a neutral compound [*vide* (*b*) above].

Hinkel and Hullin (*J.*, 1949, 1033) investigated the action of excess of aluminium chloride on the sesquichloride in the presence of benzene; they found that the double compound, m. p. 62°, of aluminium chloride with the sesquichloride (Hinkel, Ayling, and Beynon, *J.*, 1933, 674) combined with a second molecule of aluminium chloride to give a product in which the sesquichloride molecule appeared to have undergone fragmentation, and employed this product in a Friedel–Crafts reaction with benzene in the hope of obtaining evidence of a fragment $-NH{\cdot}CHCl{\cdot}NH_2$. On the assumption that the Friedel–Crafts reaction involves some process of S_N2 type :



$$Ar^- + -\overset{|}{\underset{|}{C}}-Cl \longrightarrow [Ar\cdots\overset{|}{\underset{\wedge}{C}}\cdots Cl] \longrightarrow Ar-\overset{|}{\underset{|}{C}}- + Cl^-$$

the aryl group will mark the site of the chlorine atom(s). Such a replacement would furnish a fragment $-NH{\cdot}CHPh{\cdot}NH_2$, which by subsequent hydrolysis was expected to yield benzaldehyde. Although benzaldehyde was not detected, anthracene was isolated in quantity sufficient to indicate that its formation was due to the union of two CHPh

---

* Part XVII, *J.*, 1949, 1593.

radicals, presumably derived from the fragment $-NH{\cdot}CHPh{\cdot}NH_2$ by disruption before hydrolysis.

Although the formation of anthracene affords strong evidence for the existence of the grouping $-NH{\cdot}CHCl{\cdot}NH_2$ in the sesquichloride, it cannot be said to be wholly conclusive. The Friedel–Crafts reaction with the sesquichloride has therefore been repeated with mesitylene; here the formation of an anthracene derivative is impossible, and in view of the greater reactivity of mesitylene toward aluminium chloride it was hoped to obtain a substance (VI) in which sites of all the chlorine atoms in the sesquichloride would be marked by mesityl groups. Such a compound should readily give dimesitylmethylamine (VII) and mesitaldehyde (VIII) on hydrolysis. This hope has now been realised, and provides further proof of the constitution (V) for the sesquichloride of hydrogen cyanide.

$$\underset{\text{(VI)}}{CHR_2{\cdot}NH{\cdot}CHR{\cdot}NH_2} \longrightarrow \underset{\text{(VII)}}{CHR_2{\cdot}NH_2} + \underset{\text{(VIII)}}{R{\cdot}CHO} + NH_3$$

(R = mesityl)

When an excess of aluminium chloride is added to the sesquichloride in mesitylene, the reaction product is a mixture containing *N*-(dimesitylmethyl)mesitylmethylenediamine (VI) and a substance regarded as chloro-*N*-(dimesitylmethyl)methylenediamine (IX), These compounds are readily separated through the solubility of the latter in hot water, but neither was isolated in a state of purity.

N-(Dimesitylmethyl)mesitylmethylenediamine (VI) was recognised by its hydrolysis products. It is slowly hydrolysed on steam-distillation and rapidly by hot aqueous sodium hydroxide, to give dimesitylmethylamine (VII), m. p. 96°, and mesitaldehyde (VIII); the former was characterised through its sparingly soluble mineral acid salts, and the latter was identified as the azine, m. p. 168°.

Chloro-*N*-(dimesitylmethyl)methylenediamine (IX) was recognised by its dehydrochlorination product *N*-(dimesitylmethyl)formamidine (X). By contrast with the non-basic character of compounds containing the grouping $-CCl_2{\cdot}NH-$, compounds containing the groupings $-CR_2{\cdot}NH-$ or $-CAr_2{\cdot}NH-$ exhibit basic properties and form salts, so that (X) could be isolated from the reaction mixture as the hydrochloride (XI), m. p. 181°, which is quite insoluble in organic solvents, *e.g.*, ethyl acetate:

$$\underset{\text{(IX)}}{CHR_2{\cdot}NH{\cdot}CHCl{\cdot}NH_2} \xrightarrow[-HCl]{} \underset{\text{(X)}}{CHR_2{\cdot}NH{\cdot}CH{=}NH} \longrightarrow \underset{\text{(XI)}}{[CHR_2{\cdot}\overset{+}{N}H_2{\cdot}CH{=}NH]Cl^-}$$

$$\xrightarrow[NaOH]{Aq.} \underset{\text{(XII)}}{CHR_2{\cdot}NH{\cdot}CHO} \xrightarrow[EtOH]{NaOH-} \underset{\text{(VII)}}{CHR_2{\cdot}NH_2} + H{\cdot}CO_2H$$

The elimination reaction (IX ⟶ X) occurs easily and can be brought about by dissolution of crude chloro-*N*-(dimesitylmethyl)methylenediamine (IX) in cold ethyl acetate (in which it is readily soluble) and from the hot solution in which dimesitylmethylformamidine (X) is soon deposited as the highly insoluble hydrochloride (XI). This substance is hydrolysed by aqueous sodium hydroxide to dimesitylmethylformamide (XII), m. p. 215°, which in turn is slowly hydrolysed by alcoholic sodium hydroxide to dimesitylmethylamine (VII).

When the experimental procedure (described above) is reversed—by adding the sesquichloride to three molecules of aluminium chloride, whereby the latter is always present in large excess—a different type of reaction appears largely to supervene. The main reaction now appears to involve fragmentation of the sesquichloride with subsequent reaction of the fragments with mesitylene; thus, evidence for the formation of only a small quantity of (IX) by isolation of the compound (XI) was obtained, and it is highly improbable that (VI) was produced. On the other hand, several other compounds were isolated for the formation of which no satisfactory explanation can be offered. Among the compounds isolated were two new bases, monomesitylmethylamine $C_9H_{11}{\cdot}CH_2{\cdot}NH_2$, and dimesitylamine $(C_9H_{11})_2NH$. It is probable that the former substance owes its origin to a primary Friedel–Crafts reaction of mesitylene on the single chlorine atom followed by disruption of the molecule.

The formation of the dimesitylamine is indeed surprising. This compound calls for some special comment, for unlike unsubstituted diphenylamine it displays strong basic properties, readily yielding a crystalline acetyl derivative and well-defined salts.

Hinkel and Hullin (*loc. cit.*) suggested from their experiments that anthracene was formed through a union of two $C_6H_5{\cdot}CH{:}$ fragments. In the present investigation it was also possible for the radical $C_9H_{11}{\cdot}CH{:}$ to be produced, but this cannot give rise to an anthracene grouping because of the two *o*-methyl groups, but could unite to give dimesitylethylene. A mixture of hydrocarbons was obtained consisting of an unsaturated and a saturated compound, but not in sufficient quantity for separation and identification. It is probable that the unsaturated hydrocarbon may be dimesitylethylene formed in the manner suggested, whilst the saturated hydrocarbon might be dimesitylmethane formed in a manner analogous to the production of diphenylmethane in the work of Hinkel and Hullin (*loc. cit.*).

EXPERIMENTAL

Reaction of the Sesquichloride of Hydrogen Cyanide with Mesitylene in the Presence of Aluminium Chloride.—(a) *Aluminium chloride added to the sesquichloride.* Powdered aluminium chloride (87 g., 3 mols.) was added in small portions during 0·5 hour to mesitylene (250 c.c.) containing the sesquichloride of hydrogen cyanide (35 g., 1 mol.), mechanically stirred and cooled in ice. The mixture became viscous and dark red, only a small amount of hydrogen chloride being evolved. Stirring was continued for a further 2 hours and then the mixture was allowed to regain room temperature. After 2 days the mixture separated into a dark red viscous layer with a superimposed clear layer of mesitylene. The mixture was hydrolysed by stirring it with crushed ice and concentrated hydrochloric acid. The viscous product obtained was dissolved in benzene, and the aqueous layer discarded. After the benzene and mesitylene had been removed in steam, the residue was made alkaline with 4N-sodium hydroxide and distillation continued until the distillate gave no precipitate with 2 : 4-dinitrophenylhydrazine. This aqueous distillate was extracted and the ethereal extract dried ($CaCl_2$) and evaporated, to yield mesitaldehyde. On treatment with a saturated solution of hydrazine sulphate, this gave a yellow *azine*, m. p. 168—169°, identical with a specimen prepared from authentic mesitaldehyde (Found : C, 82·0; H, 8·1; N, 9·6. $C_{20}H_{24}N_2$ requires C, 82·2; H, 8·2; N, 9·5%).

The black sticky residue in the distillation flask was drained from the alkaline solution, and then repeatedly extracted with hot dilute hydrochloric acid, until a test portion no longer yielded a precipitate on treatment with alkali. An insoluble residue (R) was examined as described below. When the hydrochloric acid extract was cooled, sparingly soluble *dimesitylmethylamine hydrochloride* was deposited as fine needles, m. p. 320° (decomp.) (Found : C, 73·3; H, 8·9. $C_{19}H_{25}N,HCl$ requires C, 73·4; H, 9·1%). Warming this with sodium hydroxide yielded the free base as an oil which readily solidified and crystallised from ethanol as fine needles of the *solvate*, m. p. 101° (Found : C, 78·9; H, 9·7; N, 4·2. $C_{19}H_{25}N,C_2H_6O$ requires C, 80·5; H, 9·9; N, 4·4%). These crystals when heated alone or kept *in vacuo* lost the ethanol and yielded anhydrous *dimesitylmethylamine*, m. p. 96° (Found : C, 84·0; H, 10·2. $C_{19}H_{25}N$ requires C, 84·2; H, 10·1%). A solution of the amine in dilute sulphuric acid, on cooling, deposited the *sulphate* as small needles, m. p. 225—226° (Found : C, 70·1; H, 8·3; N, 4·3; SO_4'', 14·7. $C_{19}H_{25}N,H_2SO_4$ requires C, 72·1; H, 8·2; N, 4·4; SO_4'', 15·1%). Addition of dilute nitric acid to a hot aqueous solution of the sulphate or hydrochloride precipitated a very insoluble *nitrate* as a white powder which decomposed without fusion at 203—204° (Found : C, 68·8; H, 7·9; N, 8·3. $C_{19}H_{26}O_3N_2$ requires C, 69·1; H, 7·9; N, 8·5%). The *acetate*, prepared in the usual way, crystallised from alcohol in large prisms, m. p. 227° (Found : C, 81·5; H, 8·5; N, 4·72. $C_{21}H_{27}ON$ requires C, 81·5; H, 8·7; N, 4·5%).

The residue R was dissolved in alcohol (charcoal) and cooled, yielding *dimesitylmethylformamide* as prismatic crystals, m. p. 215° (Found : C, 80·5; H, 8·5; N, 4·5. $C_{20}H_{25}ON$ requires C, 80·5; H, 8·7; N, 4·7%). This was hydrolysed by boiling alcoholic potassium hydroxide for several hours; dilution with water precipitated dimesitylmethylamine.

This Friedel–Crafts reaction was repeated and the procedure described followed up to the point when the benzene–mesitylene solution had been subjected to steam-distillation. As soon as mesitaldehyde was detected in the distillate, distillation was stopped. There remained a black solid residue and an aqueous solution (A). The latter was decanted and the sticky solid extracted with hot water until the extract no longer gave a deposit on cooling. The solution (A) and the aqueous extracts were combined and, on cooling, much gum separated.

After filtration and drying, the product was digested with hot ethyl acetate, which dissolved a large portion but still a residue of white material remained undissolved. This residue on repeated crystallisation from boiling water containing a little hydrochloric acid yielded *dimesitylmethylformamidine hydrochloride* as fine needles, m. p. 181° (Found: C, 72·0; H, 8·1; N, 8·6; Cl, 10·5. $C_{20}H_{27}N_2Cl$ requires C, 72·6; H, 8·2; N, 8·5; Cl, 10·7%). The ethyl acetate filtrate on slight concentration deposited a large quantity of white solid identical with the portion which could not be dissolved.

The aqueous acid filtrate from the crude dimesitylmethylformamidine hydrochloride was rendered alkaline with sodium hydroxide, the base being precipitated. This compound, which slowly evolved ammonia when moist, was steam-distilled with excess of alkali. Mesitaldehyde came over in the distillate, and the solid residue in the flask was dimesitylmethylamine.

(b) *The sesquichloride was added to the aluminium chloride.* Finely powdered aluminium chloride (50 g., 3 mols.) was added to mesitylene (200 c.c.) at room temperature, and after agitation a dark red solution resulted. The vessel was immersed in ice–salt and the sesquichloride (20 g., 1 mol.) added in small quantities during 0·5 hour. There was no evolution of hydrogen chloride but the mixture assumed a mud-like consistency and became dark reddish-brown. After 1 hour at low temperature semi-solid material separated. Stirring caused evolution of some hydrogen chloride and during 2 days the thick sludge went into solution. After a further 3 days the reaction was poured on, and stirred with, the minimum necessary amount of crushed ice and concentrated hydrochloric acid, the hydrolysis being carried out at ice–salt temperature. A viscous semi-solid mass separated, together with the mesitylene solution. The whole was extracted with benzene, and the aqueous layer containing aluminium chloride discarded. The hydrocarbon solution was shaken vigorously with water. Three layers formed, (A) the benzene–mesitylene solution, (B) a sticky portion, and (C) an aqueous layer.

Layer (B) was diluted with water and heated on a steam-bath and occluded benzene evaporated off. On cooling, a soft brown mass separated, stable to aqueous sodium hydroxide but yielding ammonia in boiling alcoholic sodium hydroxide. The solid residue after filtration was repeatedly extracted with hydrochloric acid and this extract on cooling yielded a copious precipitate of white needles, m. p. 240°. Repeated crystallisation from water containing a little hydrochloric acid gave *dimesitylamine hydrochloride* as microscopic needles, m. p. 253° (Found: C, 74·0; H, 8·2; N, 4·9; Cl, 12·4. $C_{18}H_{24}NCl$ requires C, 74·6; H, 8·3; N, 4·8; Cl, 12·3%); this gave a red colour with 90% sulphuric acid which became yellow on the addition of a trace of potassium nitrate but was unaffected by potassium nitrite. The acetyl derivative, prepared by heating the hydrochloride with acetic anhydride, crystallised from boiling alcohol as transparent prisms, m. p. 264—265° (Found: C, 80·9; H, 8·6; N, 4·9. $C_{20}H_{25}ON$ requires C, 81·3; H, 8·5; N, 4·7%).

The aqueous layer (C) was concentrated in the presence of hydrochloric acid. Dimesitylmethylformamidine hydrochloride, m. p. 181°, separated. The filtrate from the hydrochloride was made alkaline with 4N-sodium hydroxide and steam-distilled. Ammonia was evolved and volatile mesitylmethylamine distilled and solidified in the receiver. The base was converted into its *hydrochloride* which crystallised from water as fine needles, m. p. 286° (Found: C, 64·7; H, 8·6; N, 7·6; Cl, 18·9. $C_{10}H_{16}NCl$ requires C, 64·7; H, 8·6; N, 7·5; Cl, 19·1%). The *acetyl* derivative crystallised from aqueous alcohol as needles, m. p. 185° (Found: C, 75·1; H, 9·0; N, 6·9. $C_{12}H_{17}ON$ requires C, 75·3; H, 8·9; N, 7·3%).

The benzene and mesitylene were removed by steam-distillation from solution (A), and the aqueous distillate containing the last traces of mesitylene showed only a very slight test for aldehyde. The distillation was continued for a further 15 hours during which a colourless blue-fluorescent liquid was collected. The combined aqueous distillates were extracted with the benzene–mesitylene distillate, and dried ($CaCl_2$), and the extract was fractionated. The residue after the removal of the benzene and mesitylene was refractionated, first at 13 mm., yielding the following fractions: b. p. up to 75°, mesitylene, b. p. 75—87°, unsaturated to bromine water, and b. p. 87—130°. The fractionation was repeated at ordinary pressure and the following main fractions collected: mesitylene, b. p. 165°, a liquid, b. p. 198—199°, unsaturated and solid in solid carbon dioxide, and b. p. 285—300°, saturated and liquid in carbon dioxide. The amounts of these high-boiling liquids were too small for further investigation.

UNIVERSITY COLLEGE, SWANSEA.

[*Received, December* 15*th*, 1951.]