LXXVI.—*Researches on Silicon Compounds. Part VI. On Silicodiphenyldiimide and Silicotriphenylguanidine.*

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IN Part V of this series of papers (Trans., 1889, 55, 474), I described the well defined, crystalline silicophenylamide, $\text{Si}(\text{NH}\cdot\text{C}_6\text{H}_5)_4$, which proved to be the first of a new class of compounds in which silicon is exclusively united with nitrogen. In the course of the paper on the phenylamide, I pointed out that when the crystals were heated somewhat beyond their melting point, 137° , they easily lost some aniline, and added that "the residue consisted of a mixture of silicon compounds to be described later on." The nature of each of these products was, in fact, afterwards made known in the course of my Presidential Address to Section B of the British Association at Nottingham, but no details were then given, and I now desire to repair that omission preliminary to laying before the Society an account of more recent investigations.

The primary interest which attaches to the examination of the changes effected by heating the silicophenylamide is due to the probable production of silicon analogues of cyanogen compounds.

In the preliminary experiments, it was observed that about one-fourth of the total nitrogen of the anilide was easily driven off by heat in the form of aniline, and that a rather higher temperature was necessary for the removal of another fourth. At the end of this second stage, the previously fluid mass suddenly solidified, but continued heating of this residue led to the expulsion of more aniline. Of the three stages of decomposition recognised, that of solidification was most strongly marked, and therefore was first examined in detail.

Twelve grams of silicophenylamide, $\text{Si}(\text{NH}\cdot\text{C}_6\text{H}_5)_4$, were heated in a platinum boat placed in a glass tube through which a current of carefully dried hydrogen slowly passed. The gas carried with it the aniline evolved on decomposition, and the latter was condensed in a U-tube, whence it fell into a small measuring vessel. The process was stopped when the aniline collected represented half the nitrogen present in the weight of the anilide taken, and this point was found to coincide with that of the solidification of the residue already mentioned. The aniline collected contained a small quantity of a silicon compound, carried over in the current of gas and vapour.

The residue when cold was broken up and digested with carefully dried benzene, which dissolved little of the material, but removed adherent aniline, unchanged anilide, and another substance. When

purified by this treatment, the product was a white, amorphous powder, quite insoluble in benzene, light petroleum, carbon disulphide, ether, or alcohol. When heated with alcoholic solution of sodium or potassium hydroxide, it gradually dissolved with separation of aniline and evolution of a slight odour of phenyl isocyanide.

0.2912 gave 0.0816 SiO_2 . Si = 13.12.

0.351 „ 0.0993 SiO_2 . Si = 13.2.

0.263 „ 30.8 c.c. moist nitrogen at 15° and 767 mm. N = 13.76.

$\text{SiN}_2(\text{C}_6\text{H}_5)_2$ requires Si = 13.33; N = 13.33 per cent.

The nitrogen is rather high, but this was subsequently explained by the presence of traces of another compound richer in nitrogen, which is formed at an earlier stage of the decomposition, but was unknown at the time the analyses were made, and was not completely removed by benzene.

The new substance may obviously be regarded as the silicon analogue, either of diphenylcyanamide or of carbodiphenyldiimide.

The genesis of the compound from monophenylic groups and the separation of aniline, rather than diphenylamine and ammonia, on decomposition by alkalis, lead to the conclusion that it is silicodiphenyldiimide. Hence the action of heat under the conditions stated is essentially represented by the equations :

Another experiment, in which the heating of the phenylamide was stopped just short of the solidification point, gave a residue which was partially soluble in benzene. The latter solution, when evaporated, left a residue similar in appearance to the diimide and, like it, contained 13.1 per cent. of silicon, but it could not be again dissolved in benzene. Hence, an unstable soluble modification of the diimide appears to exist which easily changes into the compound which is insoluble in benzene.

As the heated amide more easily lost the first molecule of aniline than the second, it seemed probable that the following change could be realised and silicotriphenylguanidine or an isomeride be obtained.

Eight grams of the pure silicophenylamide were carefully heated as before in a current of dry hydrogen. When rather more than one molecular proportion of aniline had been collected, the decomposition was stopped, and the residue allowed to cool in hydrogen. There was no thickening of the residue while hot, but it solidified to a yellowish, transparent mass on cooling.

The product was broken up and heated with benzene. This left a small portion undissolved which possessed the characters of the diimide. The benzene solution, when mixed with twice its volume of light petroleum, gave a somewhat crystalline precipitate totally unlike the anilide obtained under similar conditions. This substance was washed with light petroleum to remove any free aniline, again dissolved in benzene, and four volumes of light petroleum were then gradually added. A precipitate formed, which was seen under the microscope to consist chiefly of droplets of a somewhat sticky substance. On standing for some hours, the liquid afforded a number of small crystals, which separated on the sides of the flask in which the precipitation was effected. These crystals were mechanically removed and purified by dissolution in benzene and subsequent separation on addition of light petroleum. This treatment involved much loss owing to the very sensible solubility of the compound in light petroleum.

The purified crystals were short prisms quite distinct in appearance from the original silicophenylamide, and much less completely precipitated from their benzene solution by addition of light petroleum. It did not afford any definite compound with acids, but was decomposed to some extent even by dry hydrogen chloride, as well as by ordinary solvents.

The crystals melted at 230° , and commenced to decompose at a slightly higher temperature; the residue did not solidify until cooled to 131° .

On analysis, the purest crystals gave Si = 9.11 and N = 14.03 per cent.

$\text{C}_6\text{H}_5 \cdot \text{N} : \text{Si}(\text{NH} \cdot \text{C}_6\text{H}_5)_2$ requires Si = 9.24; N = 13.86 per cent.

The substance is therefore a silicon analogue of a triphenylguanidine in nearly pure condition.

Hence the carefully regulated decomposition of the silicophenylamide by heat leads to the formation of

When the action of heat was studied under diminished pressure, at 16 mm., the guanidine stage was quickly passed, and the second molecular proportion of aniline carried over with it a thick liquid of high boiling point, before the residue suddenly changed to the solid diimide. This liquid was easily freed from aniline by careful heating at the low pressure maintained, and when cold was still a viscid substance. This proved to be soluble in benzene, but was precipitated in oily droplets by light petroleum, and adhered to the sides of the vessel in which the substance was thrown down. These droplets solidified after some hours, and then no longer dissolved in benzene.

The viscid liquid so obtained was the unstable form of the diimide already mentioned.

The instability of this viscid liquid suggested the possibility of its being the silicocyanamide, but its action with alkalis was that of the diimide. It is more probable that the unstable liquid represents the simple molecule of the diimide, and that the insoluble and more stable modification is a polymeric form.

When the stable form of the diimide was heated in hydrogen just short of low redness until the evolution of volatile matter ceased, a yellowish, semifused solid was obtained which did not show any charring, but this product was unable to resist a higher temperature.

This residue approximated in composition to that required by the formula

It afforded 17.54 per cent. of Si, and $\text{Si}_2(\text{N}\cdot\text{C}_6\text{H}_5)_3$ requires Si = 17.1 per cent.

It seemed probable that continued heating in presence of dry ammonia gas would facilitate the removal of the phenyl groups, and this seems to have been the case to some extent, as a residue was obtained by this treatment which was quite white, and contained Si = 32 per cent. The compound, $\begin{array}{c} \text{HN}:\text{Si} \\ \text{HN}:\text{Si} \end{array} > \text{N}\cdot\text{C}_6\text{H}_5$, requires Si = 31.7 per cent.

It was hoped that prolonged heating at a still higher temperature would remove the last phenyl group; but more or less charring occurred, hence the above represents the limit of definite change which has yet been reached by the action of heat alone on the primary substance.

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