XLVI.—*Researches on Silicon Compounds and their Derivatives.*
 Part V. *On Silicotetraphenylamide, Para- and Ortho-silicotetratolyl-*
amides, α - and β -Silicotetranaphthylamides.

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IN former communications I have shown that silicon tetrabromide can combine with several thiocarbamides without loss of halogen, and form highly condensed compounds of the type—

(Trans., 51, 203, and 53, 853).

I have now the pleasure to lay before the Society an account of certain interactions with amidic compounds in which silicon bromide and chloride lose all their halogen and afford a new class of silicon-derivatives. In the following pages I shall describe the preparation

and chief properties of five of these new substances, viz., silico-tetraphenylamide, para- and ortho-silicotetratolylamides, α - and β -silicotetranaphthylamides.

Silicotetraphenylamide.

When silicon tetrabromide is added to excess of aniline diluted with 3 to 4 vols. of benzene, much heat is evolved, and aniline hydrobromide separates out, as it is nearly insoluble in benzene. If aniline be in excess throughout the operation, the whole of the halogen precipitates as aniline salt, and there remains in solution a beautiful crystallisable compound which is silicotetraphenylamide. If the aniline be not in excess throughout the operation, a bromo-compound appears to be produced analogous to Harden's (Trans., 51, 40) rather ill-defined chlorinated product.

Silicon tetrachloride acts in a similar manner with excess of aniline and, being less costly than the tetrabromide, can be advantageously used instead of the latter in comparatively large operations. The most convenient mode of preparing considerable quantities of the new compound with the aid of the chloride will appear from the following detailed account of an experiment.

A mixture of 100 grams of silicon tetrachloride with twice the volume of benzene was gradually added to 438 grams of pure aniline, also diluted with 2 vols. of benzene. Constant agitation was maintained during the addition of the chloride, and the latter was added more slowly towards the end of the operation. The product was quickly filtered from the separated aniline hydrochloride and the latter repeatedly washed with fresh benzene. The filtrate was then distilled as far as possible from a water-bath, and finally over a naked flame at 100—105°, in a current of dry hydrogen, to remove as much benzene as possible; a syrupy liquid was left after this treatment. Experience of former preparations indicated that, while the liquid would solidify to an obscurely crystalline mass after some days, it was better to pour it still warm into an excess of carbon bisulphide, with which the syrup mixed completely. After rapid filtration from a little aniline hydrochloride, which was separated by the bisulphide, the clear solution was slowly distilled at as low a temperature as possible until reduced to the crystallising point, and it was then set aside to cool. A fine crop of large, transparent, lustrous crystals of the new compound separated, and the mother-liquors from these afforded a further supply, so that rather more than 120 grams were obtained nearly free from secondary products, of which thiocarbanilide is the most troublesome. It was subsequently found that the yield could be considerably increased by the addition of light petroleum to

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the mother-liquors, which precipitates small crystals of the tetramide from its solutions in carbon bisulphide or benzene. Two crystallisations of the best crops from fresh bisulphide yielded the new compound in a state of purity and in fine, colourless, transparent crystals, which are formed at the surface of the solution, as they are specifically lighter than the liquid. These crystals did not contain any trace of chlorine.

Products of different operations, which had been three times recrystallised from carbon bisulphide, were used in the following analyses:—

- I. 0.693 gram gave 0.103 of SiO_2 . Si = 6.93 per cent.
- II. 0.7505 gram gave 0.1115 of SiO_2 . Si = 6.93 per cent.
- III. 0.261 gram gave 32.8 c.c. of N at 16° and 751 mm. N = 14.45 per cent.
- IV. 0.23 gram gave 27 c.c. of N at 11° and 766 mm. N = 14.03 per cent.
- V. 0.2325 gram gave 0.138 of H_2O and 0.6185 of CO_2 . H = 6.59 and C = 72.55 per cent.
- VI. 0.2212 gram gave 0.127 of H_2O and 0.59 of CO_2 . H = 6.37 and C = 72.73 per cent.

These results* agree with the formula—

		Experiment.	
	Calculated.	I.	II.
Si	7.07	6.93	6.93
C	72.72	72.55	72.73
H	6.06	6.59	6.37
N	14.15	14.45	14.03

The reaction which ensues when the silicon haloïd is gradually added to excess of aniline is therefore represented by the following equation:—

which accords with the weight of hydrochloride separated in the reaction.

Silicotetraphenylamide when pure occurs in fine, colourless, transparent crystals, which have been subjected to crystallographic

* It was observed that half the nitrogen came off readily from the compound when burned with lead chromate and copper oxide, but the residue very slowly, and at the end the temperature had to be raised as high as practicable in order to ensure complete combustion.

examination by my friend Professor Sollas, F.R.S., whom I have to thank for the following statement of his results:—

“Crystalline system, oblique (monoclinic); $\beta = 110^\circ 20'$; ratio of parameters, $a : b : c = 0.9853 : 1 : 1.043$.

“The crystals consist of the following forms:—(100), (010) (111), (111), (101). The planes about the lower pole, with the exception of 001, are frequently reduced and sometimes completely suppressed,

hemimorphic crystals resulting: twins occasionally occur, with 001 as the plane of combination, and a normal to it as the twinning axis.

“The cleavage is highly perfect parallel to 001, perfect parallel to 010, scarcely perfect parallel to 100: traces of cleavage parallel to the pyramidal faces are obtainable.

“The plane of the optic axes lies in the plane of symmetry, and the acute bisectrix makes an angle of $27^\circ 20'$ with the axis c in the obtuse angle β . The apparent angle with sodium light in air is $31^\circ 5'$, and in bromonaphthalene (r. i. = 1.66) $18^\circ 36'$. A parallel sided flake obtained by cleavage along the 001 plane almost completely loses visibility when immersed in methylene iodide (r. i. = 1.7446), the mean refractive index is therefore approximately 1.7446. The true angle between the optic axes is consequently $17^\circ 40'$.

“The dispersion is inclined, p slightly less than v . The double refraction is negative.

“The extinction angle measured on the 010 plane is 7° , the edge 010, 001 being taken for reference.”

The pure compound melts at 137 – 138° to a nearly transparent liquid which can be heated in a narrow tube to 210° without decomposition.

Heated in a vacuum to its melting point, some aniline is given off,

and a mixture of silicon compounds formed whose constituents will be described later on.

Silicotetraphenylamide is very soluble in benzene but less soluble in carbon bisulphide (100 c.c. of the solution saturated at 14° contain 21.1 grams). The compound is separated from both solutions on addition of light petroleum, in which it is almost insoluble, hence in recent preparations the latter has been used with advantage in separating the pure compound. It is at once decomposed by chloroform; anhydrous ether dissolves the compound without apparent decomposition, but alcohol and water decompose it; the latter very slowly yields silicic acid and aniline. Rapid decomposition takes place if either acids or alkalis are present, especially in alcoholic solution.

So far as silicotetraphenylamide has been hitherto examined, it has not shown any distinct tendency to unite as a whole with acids, but is rather decomposed by them, even when the amide is present in considerable excess. The nature of the decomposition which takes place with hydrochloric acid appears from the results of the following experiment.

Silicotetraphenylamide was dissolved in benzene and a current of dry hydrochloric acid gas was led through it. There was immediate separation of a white substance which increased as the current of gas continued. The mixture was ultimately saturated with hydrochloric acid gas and was allowed to stand for two days; it was then filtered, the precipitate washed with benzene, and dried for analysis, during which it slightly fumed. The filtrate was not precipitated on largely diluting it with light petroleum, proving that all the silicotetraphenylamide had been separated from it. On the other hand, it contained silicon chloride in comparatively large quantity.

The precipitate was found to contain 26.51 per cent. of chlorine, but only 0.79 per cent. of silicon. It was, therefore, chiefly aniline hydrochloride from which all traces of silicon tetrachloride had not been washed out. The action of hydrochloric acid on the silicon compound is therefore represented by the equation—

There was not any evidence that a hydrochloride of silicotetraphenylamide was formed at any period of the reaction. The insolubility of aniline hydrochloride in benzene doubtless facilitated the action of hydrochloric acid.

Silicotetraparatolylamide.

At an early stage of this investigation, it was found that para- and ortho-toluidines react with the silicon haloïds in a manner similar to

aniline. As paratoluidine is most easily obtained in a state of purity, owing to the readiness with which it can be crystallised, I shall first state the results obtained with it.

To 254 grams of pure paratoluidine dissolved in benzene, 50 grams of silicon tetrachloride, also mixed with benzene, were added. An immediate separation of the hydrochloride took place, and when the whole of the reagents were mixed the hydrochloride was collected, washed with benzene, quickly dried and weighed. 170 grams of the imperfectly washed hydrochloride were obtained, whereas the following equation requires 168 grams:—

There is, therefore, practically complete separation of the hydrochloride, and nothing but the silicon compound could remain in solution. The latter had most of the benzene distilled from it, as in the case of the aniline compound; the residue was then mixed with carbon bisulphide which separated a very small quantity of hydrochloride, and the filtrate from this was then distilled down to a small bulk; on cooling it became semi-solid owing to the separation of botryoidal masses of crystals. The product was purified, with considerable loss, by pressure and recrystallisation from benzene, and was finally precipitated from its benzene solution by light petroleum and dried for analysis.

I. 0.859 gram gave 0.115 of SiO_2 . Si = 6.24 per cent.

II. 0.6192 gram gave 0.081 of SiO_2 . Si = 6.10 per cent.

III. 0.2315 gram gave 0.15 of H_2O and 0.6285 of CO_2 . H = 7.17 and C = 74.04 per cent.

IV. 0.2374 gram gave 24 c.c. of N at 12° and 767 mm. N = 12.04 per cent.

V. 0.213 gram gave 21.15 c.c. of N at 14° and 771 mm. N = 12.15 per cent.

The results* agree with the formula—

	Calculated.	Experiment.	
		I.	II.
Si	6.19	6.24	6.10
C	74.35	74.04	—
H	7.08	7.19	—
N	12.38	12.05	12.15

* The combustions were made with mixtures of lead chromate and copper oxide. As in the case of silicotetraphenylamide, the temperature required at the end was high: moreover, in the nitrogen determinations, sensibly half the gas was quickly obtained, whilst the rest came off very slowly.

Silicoparatolylamide crystallises in small botryoidal aggregations of fine needles which are colourless and transparent. They fuse at 131—132°, and decompose when more strongly heated, yielding paratoluidine. The compound is freely soluble in benzene, carbon bisulphide, and anhydrous ether, but is dissolved to a small extent only by light petroleum, which can, therefore, be used to precipitate it from its solution in the other liquids. It is decomposed by alcohol and water.

Silicotetraorthotolylamide.

In order to prepare this compound, 253 grams of pure redistilled orthotoluidine, mixed with twice its volume of benzene, was treated as in the former cases with silicon tetrachloride (50 grams) diluted with 4 vols. of benzene. Orthotoluidine hydrochloride did not begin to separate until about one-fifth of the silicon chloride had been added, as it is more soluble in benzene than the para-compound. After complete mixture of the reagents, the whole was allowed to stand over night and the hydrochloride then filtered off. The benzene was slowly distilled from the filtrate, and at the end the temperature was raised to 110°, while a current of dry hydrogen was passed over the residue to aid the removal of benzene. A thick, somewhat crystalline magma remained which was treated in the cold with carbon bisulphide. The bisulphide left 30 grams of orthotoluidine hydrochloride undissolved, which with 137 grams separated in the first treatment, gave a total quantity of 167 grams instead of the theoretical yield of 168 grams from the orthotoluidine taken, if the following equation expresses the change :—

The carbon bisulphide solution was concentrated by distillation, during which operation a further small quantity of hydrochloride separated and was removed. When heated on the water-bath until carbon bisulphide ceased to pass over, the residual liquid refused to crystallise on cooling. It was then exposed as a thin layer under the receiver of an air-pump which was frequently exhausted during 10 days, at the end of which time it gradually solidified to a crystalline mass.

In another preparation it has been found that the use of carbon bisulphide can be dispensed with, and the orthotoluidine hydrochloride can be completely removed from the benzene solution by addition of light petroleum. The silicon compound is not precipitated by light petroleum, unlike the para-derivative, and when the mixed benzene and light petroleum solution is distilled a very thick, syrupy

liquid remains, which after long exposure in a vacuum gradually yields a quantity of minute needles of the silicon compound.

When purified as completely as possible, by quick washing with light petroleum and by pressure, a specimen of the crystals gave the following analytical data:—

- I. 1·6105 gram gave 0·2204 of SiO_2 .
- II. 0·3366 gram gave 35 c.c. N at 18° and 767·5 mm.

These results agree with the formula—

	Calculated.	Experiment.
Si	6·19	6·38
N	12·36	12·06

Silicotetraorthotolylamide forms small, colourless, transparent prisms, which do not readily form aggregations. They are very easily soluble in benzene, carbon bisulphide, and light petroleum, and consequently are difficult of complete purification. Water and alcohol decompose the compound.

Silicotetranaphthylamides.

It was obviously desirable to ascertain whether double ring amidic compounds, such as the naphthylamines, interact with silicon haloids in a manner similar to those which include a single benzene nucleus. The following results prove that the two naphthylamines afford silicon-derivatives analogous to those obtained from aniline and the toluidines.

It was found that the β -naphthylamine derivative, like the paratoluidine product, was that most easily obtained in crystalline form; the α -naphthylamine derivative being even less disposed to crystallise than that afforded by orthotoluidine.

Silicotetrabetanaphthylamide was produced on the addition of a benzene solution of 10 grams of silicon tetrachloride to 67·3 grams of pure β -naphthylamine also dissolved in benzene. After separation of the hydrochloride produced in the reaction, the concentrated benzene solution was treated as already described in the other cases, and then with light petroleum, when numerous small nodular masses of slightly coloured crystals separated. These were redissolved in benzene, again separated by petroleum, collected, washed, pressed, and dried for analysis.

- I. 0·461 gram gave 0·0439 of SiO_2 .
- II. 0·3542 gram gave 29·5 c.c. of N at 18° and 768·5 mm.

These results agree fairly with the formula—

	Calculated.	Experiment.
Si	4.69	4.34
N	9.39	9.60

This compound in crystallising carries down with it some free naphthylamine which it is difficult to remove. The purest product obtained is very readily decomposed by heat, while it partially melts and assumes a brown colour. It is soluble in benzene and carbon bisulphide, but is only slightly soluble in light petroleum. Like other compounds of the kind it is readily decomposed by water.

Silicotetralphanaphthylamide was produced from α -naphthylamine by similar treatment, but unlike the β -compound it was not separated from benzene on the addition of light petroleum. When the mixed petroleum and benzene solution was evaporated, a thick, brown oil separated, and this oil, after gentle heating in a current of dry hydrogen, slowly solidified to a mass of minute crystals.

The best product yielded the following numbers on analysis:—

- I. 0.6305 gram gave 0.061 of SiO_2 . Si = 4.51 per cent.
- II. 0.2148 gram gave 16.7 c.c. of N at 20° and 766.5 mm.
N = 8.92 per cent.

Although these results show that the material was still somewhat impure, the ratio of nitrogen to silicon is 4 : 1, or that required by the formula—

The α -compound is acted on by solvents, heat, and water, even more readily than the substance afforded by β -naphthylamine, but, unlike the latter, is not separated in crystalline form by light petroleum.

I have to thank Mr. Emil A. Werner, F.C.S., for the assistance he has rendered in carrying out the work recorded in this paper

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