LXIV.—*Silicon Researches. Part XI. Silicotetrapyrrole.*

By J. EMERSON REYNOLDS.

MOST of the work recorded in former papers of this series dealt with the action of silicon halides on organic compounds which include the amino-group, such as the anilines, toluidines, and naphthylamines. In the course of the inquiry it has been shown for the first time that perfectly well-defined and often finely-crystallised substances can be obtained in which silicon is wholly combined with nitrogen. This new class of compounds, and their chief products of change, having now been sufficiently described, I propose to give an account of some similar work recently carried out with imides and nitriles.

The particular imide used was pyrrole, C_4H_5N , as its nitrogen forms part of a ring instead of merely serving for the attachment of a side-chain to a carbon ring ; moreover, it was intended subsequently to apply a synthetic reaction of pyrrole to silicochloroform, as described in Part XII (this vol., p. 508), and a preliminary examination of the action of the base with silicon tetrachloride became necessary ; the results obtained in this direction now follow.

When silicon tetrachloride and dry pyrrole are brought together, the two liquids do not mix, and no change occurs even on warming.

This indifference is in strong contrast with the violent action of aniline on the silicon halide under similar conditions. Addition of benzene, which mixes freely with both pyrrole and silicon chloride, does not lead to material interaction between the two substances ; no sensible heat is evolved, although the mixture slowly assumes a brown colour, and a brown substance gradually deposits on the sides of the containing vessel.

The examination of this brown, amorphous substance ultimately led to the conclusion that it is a variable mixture of a condensed pyrrole, chiefly tripyrrole, with an additive compound of pyrrole and silicon tetrachloride. Several preparations were made and examined, but in no case did the percentage of silicon in the dry product exceed 3.61 per cent. Apart from the incidental production of the additive compound, it is evident that direct action of silicon tetrachloride on pyrrole is somewhat similar to that of hydrochloric acid and other acids in determining molecular condensation.

As direct attack was practically useless for the replacement of the imidic hydrogen in pyrrole, an indirect method was employed, which proved to be quite successful ; this consisted in first forming potassium pyrrole, C_4H_4NK , and then acting on that substance with silicon tetrachloride.

Preparation of Potassium Pyrrole.

There is no material difficulty in the preparation of potassium pyrrole, but it is easy to destroy much expensive pyrrole in the process unless certain precautions are taken ; hence a short description of the method which afforded me the best results may prove useful to others.

Twenty c.c. of dry pyrrole were diluted with about eight volumes of a petroleum which boiled at about 110° , that is, well above the melting point of potassium. Such a mixture was gently warmed, and metallic potassium was gradually added in small, *clean* pieces, the total weight required for the above volume of pyrrole being 11 grams. The addition of each piece of the metal caused brisk evolution of hydrogen, while potassium pyrrole separated out as a fine, nearly white precipitate. During the early stages of the preparation, the flask in which the operation took place required external cooling, but at the end, the temperature was raised so as to melt the potassium in order to secure complete action—hence the use of petroleum boiling about 110° . When all metallic particles had disappeared, the potassium pyrrole was rapidly collected (using a funnel plugged with asbestos) with as little exposure to air as possible ; the precipitate was then well washed with light petroleum of low boiling point, and dried in a current of hydrogen. The slightly yellow-coloured powder so obtained

must be carefully protected from moisture; otherwise it will quickly decompose, yielding potassium hydroxide and pyrrole.

Formation of Silicotetrapyrrole.

Silicon tetrachloride acts violently on potassium pyrrole, and much pyrrole is destroyed, but when the interaction is carried out as described below, it proceeds regularly in accordance with the equation:

Twenty-one grams of potassium pyrrole in very fine powder were placed in a flask fitted with a reflux condenser, and about 100 c.c. of light petroleum (b. p. 60—65°) were added. The flask was at first immersed in a freezing mixture of ice and salt, and when sufficiently cooled, a mixture of 8·5 grams of silicon tetrachloride, diluted with 50 c.c. of light petroleum, was gradually added, the contents of the flask being freely shaken. If the addition be very slowly effected, and the temperature be well kept down by cooling, comparatively little of the brown decomposition products are obtained. The potassium pyrrole should be in excess, and at the end of the operation a gram or so of the potassium compound was added, the mixture well shaken, and then allowed to stand overnight.

The separation of the silicotetrapyrrole formed from potassium chloride was effected in a Soxhlet extraction tube provided with a good layer of dry asbestos to act as a filter. The extractor was fitted in the usual way with flask and condenser, the former containing some light petroleum; when the process of extraction was started, the boiling light petroleum dissolved the silicopyrrole compound, leaving potassium chloride. Light petroleum was found to have the great advantage over benzene and other good solvents for the pyrrole compound in that it does not dissolve the brown-coloured by-products of the interaction.

The hot light petroleum solution in the flask deposits much of its silicopyrrole on cooling in the form of small, brilliant, and nearly colourless needles, which only require recrystallisation from fresh and boiling light petroleum for complete purification. With a sample so purified, the following analytical data were obtained:

0·0962 gave 0·23 CO₂ and 0·0508 H₂O. C = 65·2; H = 5·86.

0·1167 „ 18·35 c.c. N₂ (moist) at 18° and 770 mm. N = 19·06.

0·2197 „ 0·046 SiO₂. Si = 9·77.

0·2523 „ 0·0521 SiO₂. Si = 9·62.

C₁₆H₁₆N₄Si requires C = 65·75; H = 5·48; N = 19·17; Si = 9·59 per cent.

Silicotetrapyrrole, Si(NC₄H₄)₄, when pure, crystallises from light petroleum in short, colourless prisms, but if the solution be very slowly cooled, they can be obtained from 2 to 3 cms. in length. The crystals

melt at 173.4° (corr.); if the heating be continued, the liquid gradually darkens until it becomes almost black, while a portion volatilises and condenses in crystalline form on the sides of the tube in which the melting-point determination is carried out.

The substance is only slightly soluble in cold light petroleum, but is much more soluble in the boiling liquid. It is easily soluble without change in benzene, chloroform, or carbon disulphide. Anhydrous ether dissolves it without apparent decomposition; it is also soluble in absolute alcohol, but with ultimate decomposition.

The easy solubility of the compound in benzene, and the stability of the solution, rendered that solvent suitable for the determination of the molecular weight of the silicon compound by the boiling-point method. The data obtained, using a Beckmann's special thermometer, were as follows:

0.5304, in 13.187 benzene, gave Δt 0.37° ; whence M.W. = 290.

$C_{16}H_{16}N_4Si$ requires M.W. = 292.

A similar determination of the molecular weight of silicotetraphenylamide gave 402, instead of 396 as required by the formula $Si(C_6H_5)_4$. There is therefore no doubt that both the pyrrole and the phenylamine silicon compounds exist as simple molecules in boiling benzene solution.

Silicotetrapyrrole is a comparatively stable substance in the absence of moisture and air. It does not give off pyrrole on heating until the temperature is so high that the material carbonises; and no such intermediate changes appear to take place as those observed and examined in the case of the compound $Si(NC_6H_5)_4$. This greater fixity is doubtless due to the fact that each nitrogen atom forms part of a pyrrole ring, and is externally combined only with silicon.

THE DAVY-FARADAY LABORATORY,
ALBEMARLE STREET,
LONDON,