

cises an even valence, as in $C_5H_5N \left\langle \begin{smallmatrix} R \\ I-I \end{smallmatrix} \right.$, or perhaps $C_5H_5N \left\langle \begin{smallmatrix} R \\ I=I \end{smallmatrix} \right.$. With the higher perhalides the burden of experiment points very strongly to the formation of compounds having only an even number of additive halogen atoms. The

structure may be $C_5H_5N \left\langle \begin{smallmatrix} R \\ I \left\langle \begin{smallmatrix} I-I \\ | \\ I-I \end{smallmatrix} \right. \right. \end{smallmatrix} \right.$, etc., at all events indicating uneven valence for all halogen atoms. It is quite probable that all the pyridine perhalides exist in monopyridine molecules.

If there be an analogy between the perhalides of the tertiary amines and the ammonium salts of the oxyacids of chlorine, then

the structure may be $\equiv N \left\langle \begin{smallmatrix} R \\ (I=I)-I \end{smallmatrix} \right.$, $\equiv N \left\langle \begin{smallmatrix} R \\ (I=I)-I \left\langle \begin{smallmatrix} I \\ | \\ I \end{smallmatrix} \right. \right. \end{smallmatrix} \right.$,

etc., where $(I=I) = O$. In this case the single additive halogen would be divalent and a substitute for oxygen, *i. e.*, $\begin{smallmatrix} H \\ H \end{smallmatrix} \equiv N \left\langle \begin{smallmatrix} H \\ O-Cl \end{smallmatrix} \right.$ and $\equiv N \left\langle \begin{smallmatrix} R \\ I-I \end{smallmatrix} \right.$. In the mixed perhalides to be reported in a later paper, the single additive halogen is of more frequent occurrence.

I wish to express my thanks to Professor A. B. Prescott, to whom I have gone for advice and under whose general supervision the work has progressed; also to Messrs. O. C. Diehl² and R. E. Knapp for their assistance in the laboratory.

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MODIFICATION OF THE THALLEOQUIN TEST FOR QUININE.

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IT is extremely important for the success of this test that the reagents employed should be dilute. Some authorities give the quantity of each reagent necessary, without stating the proper dilution, thereby causing much inconvenience.

The light green coloration produced on porcelain by contact of the quinine salt with weak bromine or chlorine water and

¹ This Journal, 17, 780.

² This is the beginning of Mr. Diehl's work upon "Foundations for the Estimation of Alkaloids. Conducted for the Committee of Revision of the U. S. Pharmacopeia," by Prof. A. B. Prescott. The next following work has been upon "Mixed Perhalides of Pyridine and Piperidine," now nearly ready for publication.

ammonia is not nearly so striking as the brilliant emerald green color obtained by using dilute solutions in a test-tube.

Usually, the analyst deals with unknown quantities, or mere traces, but, for experiment, it will be found convenient to use from three to five milligrams of the quinine salt for each test. (With larger amounts there is a tendency to form bulky precipitates.)

For example, place three to five milligrams (0.003-0.005 gram) quinine sulphate in a test-tube and add about five cc. distilled water. Acidulate with *one* drop (not more) of dilute sulphuric acid (1 : 4) which immediately dissolves the quinine sulphate with a blue fluorescence. An excess of the acid should be avoided.

At this point various authorities recommend the addition of weak bromine or chlorine water ; but the writer has found that if a clear, filtered solution of calcium hypochlorite (bleaching powder) be substituted for the bromine or chlorine water, the results will be more satisfactory so far as certainty and brilliancy of the test are concerned.

The points to be observed are as follows : After acidulation with one drop of sulphuric acid (1 : 4), the hypochlorite solution is added through a small filter to the quinine solution in the test-tube, until the blue fluorescence just disappears, and the solution acquires a faint golden tint ; then add a few drops of dilute ammonia (1 : 3) when a clear emerald green color should appear. (Thallesquin test.)

The tint, thus produced, seems to be more brilliant than that obtained through the agency of bromine water.

On the addition of a slight excess of dilute sulphuric acid to this green solution, a blood-red tint will be produced which may be considered confirmatory. This is not always the case, however, when bromine water has been used in the preliminary operation.

Potassium or sodium hypobromite is not applicable on account of the strong alkali which tends to precipitate the white quinine base and thus interfere with the brilliancy of the test. Chlorinated soda (Labarraque's solution) likewise gives uncertain results, the tints varying from yellowish-green to violet.