group the high valence oxides of elements of lower atom number are more stable than corresponding ones of higher atom number is clearly brought out in the ruthenium and osmium rows. OsO_4 and RuO_4 are the only octavalent oxides known, while even the lower oxides of platinum and palladium are very unstable. Potassium perrutheniate $KRuO_4$ is closely analogous to potassium permanganate, though not isomorphous.

(11) Another very striking argument for placing manganese in the eighth group can be found in the fact that alloys of manganese with iron, cobalt and nickel show no tendency to compound formation, while manganese forms compounds stable at the melting point with almost all the metals of lower groups including chromium, vanadium, and silicon.[1] Apparently the alloys of manganese with titanium have not been studied.

(12) The manganese compounds with the metalloids such as carbon and silicon are analogous to those of iron and not to those of chromium.

(13) The atom colors of the various valences of manganese show that the normal valence of manganese must be even, not odd, as the position in the seventh group would require.[2]

Summary.

(1) The older arguments placing manganese in the seventh group of the periodic system (*i. e.*, giving manganese a normal valence of 7) now appear open to question.

(2) On the other hand there are 12 different lines of argument based on purely chemical relationships which indicate its position in the eighth group.

(3) This conclusion is also in accord with the more decisive reasoning based on atom color.

(4) An improved form of the Periodic Table showing the relations of the eighth and rare earth groups to the rest of the periodic system is presented.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONSTITUTION OF DICYANODIAMIDE.[3]

BY WILLIAM J. HALE AND FRANK C. VIBRANS.

Received February 23, 1918.

Upon the evaporation of an aqueous solution of cyanamide, Beilstein and Geuther[4] obtained a colorless product which they supposed to be a

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[1] Guertler, *Metallographie* (Berlin), I, see index (1912).

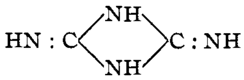
[2] Bichowsky, THIS JOURNAL, **40**, 500 (1918).

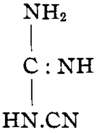
[3] The work described in this article forms part of a thesis submitted by Frank C. Vibrans in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[4] *Ann.*, **108**, 99 (1858); **123**, 241 (1862).

polymeric form of cyanamide. This so-called "param" (paracyanamide) was later named dicyanodiamide by Haag[1] but no mention of its probable constitution was made till Hallwachs[2] attempted to substantiate the Formula I as put forth by Strecker in his text book on organic chemistry (5th edition, 1867, p. 637). A few years later Baumann[3] studied the action of acids and alkalies upon dicyanodiamide and interpreted the results as proceeding directly from this same ring structure.

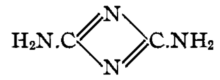
In 1880 Bamberger[4] proposed the cyanoguanidine structure (II) for dicyanodiamide


(I).



$$\begin{array}{c} \mathrm{NH_2} \\ | \\ \mathrm{C:NH} \\ | \\ \mathrm{HN.CN} \end{array}$$

(II).


(III) (a tautomer of I).

a consideration arising out of no material evidence unless the decomposition of dicyanodiamide into ammonia and carbon dioxide, and the further condensation between carbon dioxide and original substance at 160–170° into melanuric acid, can here be cited. However, the Bamberger formula, that of guanidine in which a cyanogen group replaces one hydrogen of an amino group, is admirably adapted for interpretation of all reactions in which dicyanodiamide is concerned. The action of water,[5] hydrogen sulfide,[6] ammonia[7] and other reagents are considered as affecting primarily this cyanogen group. In the same manner Rathke[8] explained the action of carbon dioxide and also that of thiocyanic acid as attacking directly this cyanogen group of dicyanodiamide. The inadequacy of these explanations as advanced by Rathke, led Klason[9] to propose a third structure (III) as the more probable formula for dicyanodiamide. Hofmann[10] also supported this view expressed by Klason.

Somewhat later Bamberger[11] investigated the production of ammeline by the action of cyanic acid upon dicyanodiamide and came to the conclusion that cyanic acid, thiocyanic acid, or carbon dioxide must be considered as involving primarily the free amino group. Here also Bam-

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[1] *Ann.*, **122**, 22 (1862).

[2] *Ibid.*, **153**, 293 (1870).

[3] *Ber.*, **6**, 1374 (1873); **7**, 447 (1874); **8**, 708 (1875).

[4] *Inaugural Dissertation*, Berlin, **1880**; *Ber.*, **16**, 1074 (1883).

[5] *J. prakt. Chem.*, [2] **1**, 288 (1870).

[6] *Ber.*, **11**, 962 (1878).

[7] *Monatsh.*, **1**, 88 (1880).

[8] *Ber.*, **18**, 3105 (1885).

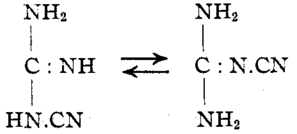
[9] *J. prakt. Chem.*, [2] **33**, 116 (1886).

[10] *Ber.*, **18**, 2782 (1885); **19**, 2086 (1886).

[11] *Ibid.*, **20**, 68 (1887); **23**, 1856 (1890).

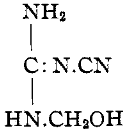
berger and Seeberger[1] introduced the fact that piperidine and dicyanodiamide combined to form a substituted biguanide as evidence in support of Formula II. Though this proof was by no means conclusive, later work by Bamberger[2] on certain reduction products would seem to corroborate his early assumptions.

Through these additive reactions, involving either the cyanogen or the amino group, the constitution of dicyanodiamide seemed almost established. Reactions, however, in which 2 of the groups in this compound might jointly be involved in a condensation, such as with acetoacetic ester, were not studied until 1908, when Pohl[3] undertook the investigation, and at the same time endeavored further to gain direct information concerning the possible number of amino groups in this compound by a study of its decomposition with sodium hypobromite. The results here indicated the evolution of slightly more than one-half of the total nitrogen in the molecule and, assuming that the amino group only can react to this end, Pohl at once proposed for dicyanodiamide a new and fourth formula (IV) tautomeric with the cyanoguanidine, Formula II. The condensation of formaldehyde with dicyanodiamide was here considered as proceeding directly from a compound of Formula IV and resulting in a product as shown in (V). On the other hand acetoacetic ester was considered as reacting only with that compound of type (II) and resulting in a product as shown in (VI), 2-cyanamino-4-methyl-6-hydroxypyrimidine.



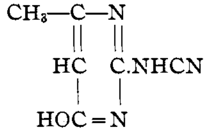
$$\begin{array}{c} NH_2 \\ | \\ C:NH \\ | \\ HN.CN \end{array} \rightleftarrows \begin{array}{c} NH_2 \\ | \\ C:N.CN \\ | \\ NH_2 \end{array}$$

(II). (IV).

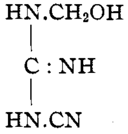


$$\begin{array}{c} NH_2 \\ | \\ C:N.CN \\ | \\ HN.CH_2OH \end{array}$$

(V).



(VI).



$$\begin{array}{c} HN.CH_2OH \\ | \\ C:NH \\ | \\ HN.CN \end{array}$$

(VII).

No reasons were advanced by Pohl to substantiate his assumption that a primary amine group evolves nitrogen when interacting with hypobromous acid. This is to be regretted inasmuch as one usually interprets the reaction of hypobromous acid upon primary amines as leading directly to alkyl mono- or di-halogen amines. A monohalogen amine in juxtaposition to a carbonyl group, *i. e.*, a monohalogen amide, readily undergoes the Hofman transformation in the presence of alkali to give an amine with one less carbon atom. Of course the action of hypobromous acid upon a diamino compound such as hydrazine will give nitrogen by oxidation. Even a mild alkali is sufficient for the hydrolysis of dicyanodiamide into cyanurea and ammonia and this latter, through

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[1] *Ber.*, **24**, 899 (1891).

[2] *Ibid.*, **16**, 1461 (1883); **26**, 1585 (1893).

[3] *J. prakt. Chem.*, [2] **77**, 533 (1908).

oxidation by the hypobromite, would account for the first nitrogen atom liberated; Pohl's experiments have indicated that a volume of nitrogen corresponding to one nitrogen atom in the molecule of dicyanodiamide is always liberated in the first few minutes of the reaction, whereas several hours must elapse for the liberation of the rest of the gas. It is surprising however, that Pohl did not recognize the transformation which cyanurea itself might undergo in its reaction with hypobromous acid, resulting in the liberation of 2 more nitrogen atoms and an alkali cyanide as end product. We have found indeed that any metallic cyanide, introduced in this alkaline solution, will fail to give up its nitrogen under the conditions of this experiment. It should be possible, therefore, for one to obtain exactly three-fourths (in place of the one-half erroneously assumed by Pohl) of the total nitrogen in dicyanodiamide by the action of an alkali hypobromite or hypochlorite. In repeating the experiment, as outlined by Pohl, we have attained this value, *i. e.*, 51.3% instead of the theoretical 50% of the molecular weight of the compound. Sodium hypochlorite in 20% solution was employed in place of the 10% calcium hypochlorite used by Pohl. With the latter concentration Pohl obtained 38% of nitrogen. The use of sodium hypobromite, however, gave him about 35.2% and this value was chosen as more closely approaching the anticipated 33.3%, or one-half of the 66.7% which represents the total amount of nitrogen in the molecular weight.

In order to check our results on the action of alkaline hypochlorite solution in liberating all of the nitrogen in dicyanodiamide save from the cyanogen group, and thus finally to dispose of any theory maintaining that exactly one-half of the nitrogen exists, or is possible of existence, in the same group arrangement, it became necessary for us to apply some method for the determination of a primary amine group. This method then must be applied to the formaldehyde addition product of dicyanodiamide (V), as prepared in the manner directed by Pohl, and the presence of the free amino group, herein demanded by Pohl's formula, once and for all disproved. As this formaldehyde condensation product was found to be readily hydrolyzable by hot water, the method for determining free amino groups must involve the use of almost anhydrous solvents.

The use of nitrous acid seemed to offer the best means at our disposal for the determination of an amino group. The method first devised by Sachsse and Kormann[1] and later much improved by D. D. Van Slyke[2] was at once applied to this study. When samples of dicyanodiamide, or its formaldehyde condensation product, were introduced into the Van Slyke apparatus and the operations conducted with the greatest care,

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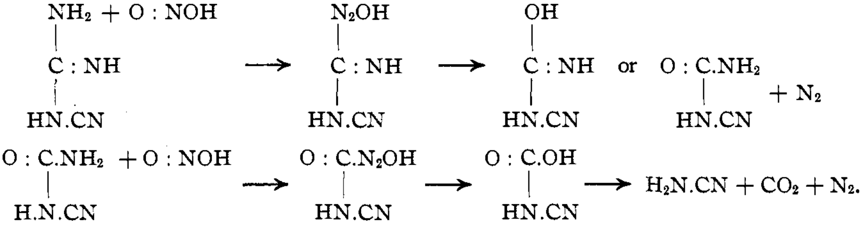
[1] *Z. anal. Chem.*, 14, 380 (1875).

[2] *J. Biol. Chem.*, 9, 185 (1911); 12, 275 (1912).

no nitrogen whatever was evolved. No doubt the condensation product was hydrolyzed in the 50% acetic acid used as solvent. In any event dicyanodiamide must be considered as unreactive toward nitrous acid under these conditions. In fact several amino derivatives have been reported by Van Slyke as failing to give nitrogen by interaction with nitrous acid. Dicyanodiamide consequently would fall in this class along with guanidine and others. Believing, however, that a reaction could be produced at higher temperatures, a different form of the apparatus was employed and a number of experiments performed, with the result that dicyanodiamide, and even guanidine, came into the reaction. Carbon dioxide was now used to displace the air from the apparatus, and the acid mixture in the reaction flask brought almost to boiling before the sodium nitrite was introduced. The well-known reaction of nitrous acid upon primary amines, resulting in the substitution of the amino group by hydroxyl, through the loss of nitrogen from the intermediate diazo compound, must also be related to the reaction of nitrous acid upon amino groups which are not attached to carbon atoms; in this latter reaction nitrous oxide is evolved. Dicyanodiamide at all events comes under the first classification and the action of nitrous acid should lead only to the formation of one diazo complex and thus to the elimination of one atom of nitrogen per molecule of compound. If at any time dicyanodiamide could rearrange itself into a type of strong base as represented by Formula IV then nitrous acid should react with both of the amino groups, therein represented, and 2 atoms of nitrogen should be eliminated from one molecule of the compound; in other words one-half of the total nitrogen available should be liberated at the same conditions which make for the liberation of any nitrogen whatsoever.

The use of a 50% acetic acid solution, such as is recommended by Van Slyke, was first tried under the new conditions, namely, at the boiling temperature of the acid mixture. As a result there was obtained but one-fourth of the nitrogen represented by the loss of a single nitrogen atom per molecule of dicyanodiamide. The use of glacial acetic acid itself gave no uniform results but indicated the loss of at least 3 nitrogen atoms from the molecule. A solution consisting of 85% glacial acetic acid and 15% water gave the best results. Here only one nitrogen atom was liberated. At a concentration of 95% acetic acid 2 nitrogen atoms were liberated and by use of 85% phosphoric acid all of the nitrogen could be liberated. The temperature, and the concentration of the acid were found therefore to play the important role in this manner of decomposition. The ease with which the first nitrogen can be eliminated (using 85% acetic acid) with its consequent production of cyanurea in the reaction mixture, is decidedly marked in comparison with the decomposition of cyanurea into a cyanocarbamic acid. From the latter compound, possibly as cyanamide, another nitrogen is liberated and finally even the cyano group may be made to yield its nitrogen. It is possible of course that at the higher temperature, necessary for this last step, little hydrolysis is possible and the decomposition of any cyanamide may proceed to completion but only at a slow rate; the lack of uniformity in the results obtained with anhydrous solvents would lead at least to this inference.

From the work of Werner[1] it is clear that urea itself reacts with nitrous acid only when in the presence of an acid sufficiently strong to produce a salt of the type $HO.C(:NH).NH_2.HX$; the amino group, thereby presented, constitutes the point of attack for nitrous acid. If cyanurea is the first product resulting from the action of nitrous acid upon the dicyanodiamide, it would naturally follow that cyanocarbamic acid (and thus cyanamide) would result in the next instance. Cyanamide forms very stable salts with acids but these salts eventually would be brought into action with nitrous acid under the influence of stronger mineral acids and all of the nitrogen thus liberated.



$$\begin{array}{l}NH_2 + O:NOH \\ \quad | \\ C:NH \\ \quad | \\ HN.CN\end{array} \longrightarrow \begin{array}{l}N_2OH \\ \quad | \\ C:NH \\ \quad | \\ HN.CN\end{array} \longrightarrow \begin{array}{l}OH \\ \quad | \\ C:NH \\ \quad | \\ HN.CN\end{array} \text{ or } \begin{array}{l}O:C.NH_2 \\ \quad | \\ HN.CN\end{array} + N_2$$

$$\begin{array}{l}O:C.NH_2 + O:NOH \\ \quad | \\ H.N.CN\end{array} \longrightarrow \begin{array}{l}O:C.N_2OH \\ \quad | \\ HN.CN\end{array} \longrightarrow \begin{array}{l}O:C.OH \\ \quad | \\ HN.CN\end{array} \longrightarrow H_2N.CN + CO_2 + N_2.$$

The investigation conducted by Werner[2] support indeed this conclusion that amino groups may be made to react with nitrous acid if the acid solvent is of sufficient strength. Dicyanodiamide undoubtedly possesses one amino group, as is evidenced by the comparative ease with which the first nitrogen-containing group is attacked. If a second amino group is present its interaction with nitrous acid should proceed under practically these same conditions. The development of a second amino group in the course of the decomposition might therefore account for the higher temperature and longer time necessary for interaction with a second molecule of nitrous acid. Certain it is that a free amino group may be made to interact readily with nitrous acid under the conditions as described by us. We have failed so far to find a compound possessing an amino group which does not thus interact. The negative results obtained by Van Slyke with guanidine are undoubtedly due to the dilute acetic acid (at room temperature) as employed in his work. We had only to verify our assumptions by a few reactions with guanidine under the conditions we describe. When guanidine carbonate is decomposed by

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[1] *J. Chem. Soc.*, 111, 863 (1917).

[2] *Loc. cit.*

nitrous acid in 50% acetic acid no nitrogen is liberated, as correctly reported by Van Slyke.[1] However in hot glacial acetic acid solution 2 nitrogen atoms are liberated, and even in higher boiling acids, such as isobutyric acid, no more than the 2 nitrogen atoms could be liberated from one molecule of substance. It is possible that the imino group in guanidine, possessing such strong basic properties, still remains intact in all of our acid mixtures; the 2 primary amine groups however appear to react as normal.

The further application of this method for reactions with nitrous acid, was now to be applied to the dicyanodiamide formaldehyde condensation product of Pohl. When glacial acetic acid was employed here as solvent the condensation product decomposed exactly as did dicyanodiamide itself and 3 nitrogen atoms per molecule were set free. When, however, those conditions were maintained under which dicyanodiamide lost but one atom of nitrogen (*i. e.*, with 85% acid) we found scarcely any nitrogen at all liberated from this condensation product; and this notwithstanding the fact that water acts readily in its hydrolysis. If the operation were made to extend through an unusual length of time a few cc. of nitrogen could be obtained, but this of course was due to a slow hydrolysis of the product. We conclude therefore that the formaldehyde condensation product of Pohl possesses no such structure as that assigned by him, but, in the event that no ring structure is developed, the formula accords with a structure as in (VII), where the one free amino group of dicyanodiamide is considered as having entered into condensation with formaldehyde.

From the reactions just studied with compounds containing 2 or more nitrogen atoms it is clear that little or no evidence can be gained on the possible reactivity of those amino or amido groups in the products left after the removal of one amino group; this primarily by reason of the varying degree of basicity among these products themselves, thus necessitating the employment of stronger and stronger acids to effect the salt formation which is preliminary to the reaction with nitrous acid. At the point where dicyanodiamide and nitrous acid begin to react we can indeed secure the liberation of nitrogen which corresponds only to one nitrogen atom in the molecule of dicyanodiamide. The next and closely following steps in this reaction with nitrous acid necessarily prohibit any very definite conclusions in regard to what other nitrogen groups may have been present in the original molecule. The assumption that dicyanodiamide might exist in a tautomeric form (IV) was advanced by Pohl without experimental evidence; but if at any time a structure of a diamino derivative were existent then the very best conditions would be extended for condensation with diketones to form pyrimidines. We

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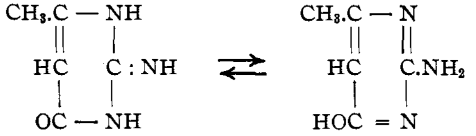
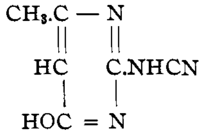
[1] *Loc. cit.*

have chosen therefore to establish the constitution of dicyanodiamide as existing alone in the cyanoguanidine form (II) by a detailed study of the manner of its condensation with β-diketones. The work of Köhler[1] upon the reaction of guanidine and acetoacetic ester is looked upon as leading to 2 possible types of compounds (VIII) and (IX) which possibly exist together as tautomers.



(VIII). (IX).



(X).

Pohl believed that dicyanodiamide, as cyanoguanidine, should condense with acetoacetic ester to give a compound of Formula X, 2-cyanamino-4-methyl-6-hydroxypyrimidine. It was Pohl's purpose to determine definitely the position of the cyano group in this pyrimidine and in this he succeeded in establishing its position as above shown (X). A 10% hydrochloric acid solution readily transformed the cyanamino group to an ureido group, and this in turn by further action of conc. hydrochloric acid at 125° lost one molecule of ammonia and one of carbon dioxide, and there remained a free amino group: the final product thus identical with the compound (IX) or 2-amino-4-methyl-6-hydroxypyrimidine of Köhler. The tautomeric form for dicyanodiamide (IV) is still to be considered, and consequently Pohl could not have decided by this work whether after all his diamino Formula IV had or had not been concerned in the reaction. Had this condensation proceeded from a compound of the diamino type then a cyanimino pyrimidine would have resulted, and this upon saponification of the cyano substituent could have yielded only that same product obtained by Köhler, now in its tautomeric form (VIII), a 2-imino-4-methyluracil, a point leading to no very definite conclusions regarding the original structure of dicyanodiamide.

We selected therefore to study a condensation of dicyanodiamide with a β-diketone, or a compound which carried alkyl groups more or less fixed in their position at either end of the —CO.CH$_2$.CO— complex. The simplest example available is acetylacetone. In practically all of the instances where this diketone condenses with basic substances to ring formation, it is necessary to regard it as reacting in enolic form. Thus acetylacetone and guanidine were shown by A. and C. Combes[2] to condense to a 2-amino-4,6-dimethylpyrimidine (XI).

Majima[3] has reported that methylguanidine condenses with acetoacetic ester in two different ways, depending upon the fact whether or not the

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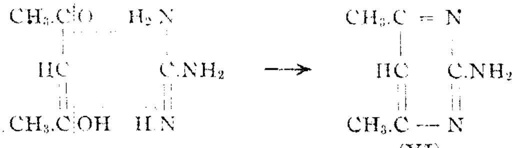
[1] *Ber.*, **19**, 220 (1886).

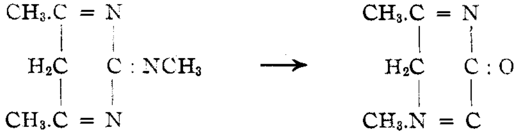
[2] *Bull. soc. chim.*, [3] **7**, 791 (1892).

[3] *Ber.*, **41**, 176 (1908).

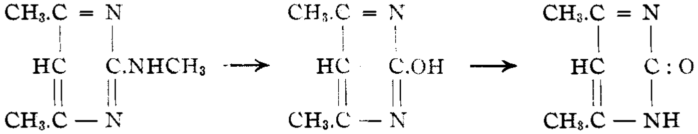


(XI).

amino group containing the methyl substituent is directly involved in the ring closing. With acetylacetone, on the other hand, only one product was obtained and this was considered by Majima as possessing the constitution (XII). When the compound was heated to 160° with conc. hydrochloric acid there resulted the so-called acetylacetoneurea of Evans[1] (XIII). From the work of one of us[2] it would seem that the generally accepted formula for methylguanidine should here be accepted and the condensation explained upon the enolic form of acetylacetone. The product (XIV) may accordingly be looked upon as a simple derivative of the acetylacetoneguanidine (XI) of A. and C. Combes, and naturally the loss of methylamine through the action of concentrated acid would lead directly to the more stable or imino formula for acetylacetoneurea (XV).

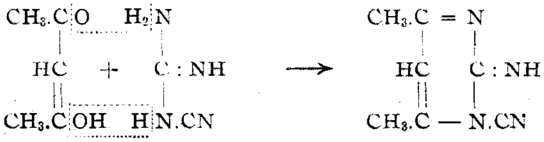


(XII). (XIII).



(XIV). (XV).

A condensation between acetylacetone and dicyanodiamide may now be considered from the several standpoints or possibilities afforded in the various formulas proposed for the latter. From data already given and from further considerations before us we may exclude the 2 ring structures and consider only Formulas II and IV. The manner in which these several condensations may proceed is indicated below; sodium hydroxide served throughout as the condensing agent.



(II). (XVI).

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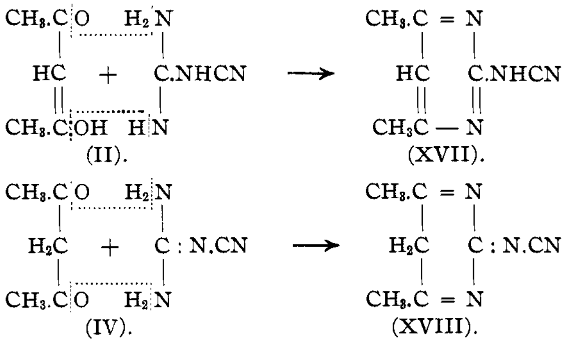
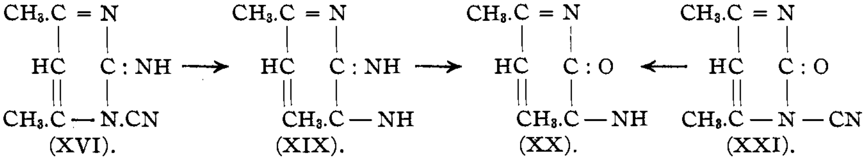
[1] *J. prakt. Chem.*, [2] **48**, 489 (1893).

[2] THIS JOURNAL, **36**, 104 (1914).



(II). (XVII). (IV). (XVIII).

The final product accorded with the analysis for $C_7H_7N_4$; upon application of the Liebermann and also the Hinsberg test the presence of a secondary amine was clearly indicated. The Hofmann isocyanide test for a primary amine failed altogether. These characteristic indications alone point to the absence of any compound of type (XVIII) and hence give no support to a diamino structure for dicyanodiamide. When the condensation product was treated for several hours with hot dil. (1 : 5) sulfuric acid, the cyanogen group was saponified and carbon dioxide and ammonia liberated. The product remaining in the acid solution was then removed and found to analyze for $C_6H_9N_3.H_2O$. This new product again gave positive results with both the Liebermann and the Hinsberg tests for secondary amines, and failed to show the presence of any primary amine through the isocyanide reaction. If now the original condensation product possessed a constitution as shown in (XVII) then the loss of the cyano group through saponification would lead directly to the aminopyrimidine (XI) of A. and C. Combes. The final product, however, is not identical with the aminopyrimidine of Combes, and further the indications are apparent that no primary amine is at hand. The conclusion is then to be drawn that our condensation product accords with a formula as shown in (XVI). This by simple saponification of its cyanogen group would yield a new compound, an iminopyrimidine, of Formula XIX.



(XVI). (XIX). (XX). (XXI).

The qualitative tests indicative of a secondary amine are now explicable. This new product may be made to lose another molecule of ammonia by the action of a hot sodium hydroxide solution. The reaction mixture, upon evaporation, yielded the well-known and characteristic crystals of acetylacetoneurea (XV) or again as shown in (XX). The action of strong alkali is thus seen to accomplish the removal of the imino group with its replacement by oxygen, whereas dilute acids sufficed only for the saponification of the cyanogen group.

The aminopyrimidine of Combes (XI) can be converted into acetylacetoneurea by the action of strong acid. It does not, however, evolve ammonia so readily at its melting point (153°) as does the iminopyrimidine at similar point (199°). The 2 compounds therefore are in no way identical. With the imino- and the amino-pyrimidines thus distinguished there remains but one conclusion: the original condensation product must have a structure as represented in Formula XVI and accordingly should be considered as an iminopyrimidine.

It was thought that through the action of a mild alkali upon the original condensation product we might be able to remove the imino group alone and prepare a product as shown in (XXI), a 1-cyano-2-keto-4,6-dimethyl-1,2-dihydropyrimidine. The reaction undoubtedly proceeded as expected. The production of no carbonate in the reaction mixture indicated that the cyanogen group was still intact, but at no time was there anything like an equivalent of one nitrogen evolved as ammonia. The product isolated from the reaction mixture consisted of a mixture of the hoped-for cyanopyrimidine together with the original condensation product yet unacted upon. When this mixture was treated with dil. (1 : 5) sulfuric acid an appreciable quantity of acetylacetoneurea (XX) was always produced, thereby indicating that the cyanopyrimidine must have been present in the mixture; the original product, or imino-cyanopyrimidine, failing to give any acetylacetoneurea under these conditions. Attempts were now made to prepare this cyanopyrimidine (XXI), by condensing acetylacetone directly with cyanurea. The condensation, however, could be brought about only in acid solution, and there resulted acetylacetoneurea. Whether or not the condensation had preceded or succeeded the saponification of the cyanogen group could not be ascertained. Finally, that product which may be considered as the half saponified cyanurea, namely, biuret, was also brought into condensation with acetylacetone. Here, too, acids alone constituted the only means effective for condensation and again the result was acetylacetoneurea.

There seemed therefore no possibility of our preparing directly either the cyano- or the amido-acetylacetone-urea, those compounds which would have served admirably in checking some of our intermediate steps in this investigation. The work of Combes, however, is sufficient by itself in indicating the only other end course which our condensation could have taken. In that we can find no such product as he describes it remains for us to accept the alternative or that course which will lead to the same end product, acetylacetoneurea, but without involving the same intermediate step. We conclude, therefore, that our original condensation product must be represented as in Formula XVI and that the constitution of dicyanodiamide must accord only with that formula (II), as represented by Bamberger.

Experimental Part.

The acetylacetone employed in this investigation was prepared according to the directions of Claisen and Ehrardt.[1] The dicyanodiamide was prepared as follows:

Dicyanodiamide.—One kg. of calcium cyanamide (nitrolime) was suspended in 2 liters of water and heated for an hour upon a steam bath. The final solution was then filtered by suction and the residue washed with water. To the combined filtrates a few cc. of ammonium hydroxide solution was added in order to facilitate the transformation of the free cyanamide into dicyanodiamide. The ammoniacal solution was then evaporated to about 500 cc. in volume and allowed to cool. The large rhombohedral crystals of dicyanodiamide soon separated; a recrystallization of the product from water gave finally 130 g. of pure product, m. p. 205°. Dicyanodiamide is fairly soluble in water, alcohol or acetone; slightly soluble in ethylacetate; and insoluble in ether, chloroform, benzene, carbon tetrachloride, carbon disulfide or ligroin.

The Action of Hypochlorous Acid upon Dicyanodiamide.—The work of Pohl[2] indicated that 2 nitrogen atoms could be removed from one molecule of dicyanodiamide by this manner of oxidation. The total nitrogen in dicyanodiamide calculates to 66.67% of the molecular weight. When a dilute solution of sodium hypobromite was allowed to act upon dicyanodiamide Pohl found that 35.2% of nitrogen was evolved. With calcium hypochlorite (bleaching powder) 38% was evolved. From this he assumed one-half (35/66ths) of the nitrogen could be removed. We find that with calcium hypochlorite 0.0168 g. of dicyanodiamide gave 5.6 cc. of nitrogen, calculated to 0° and 760 mm. This result calculated to a higher percentage of nitrogen than obtained by Pohl but is not quite sufficient for three-fourths of the total nitrogen, or that represented by the loss of 3 atoms of nitrogen per molecule of compound. We now used a 20% sodium hypochlorite solution and found that the reaction proceeded to completion in 6–8 hours. 0.0168 g. dicyanodiamide gave 6.9 cc. nitrogen, calculated to 0° and 760 mm. The theoretical volume of nitrogen obtainable from this weight of substance at the standard conditions, and representative of all 4 nitrogen atoms in one molecule, is 8.96 cc. Our result therefore indicates that 6.9/8.96 or 77% of this possible value is easily liberated; the conclusion is decisive; 3 atoms of nitrogen can be removed from each molecule by this manner of oxidation. By reference to Pohl's method of calculation 6.9 cc. represents 51.3% of the molecular weight, of which 66.7% is nitrogen. Accordingly 51.3/66.7 or three-

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[1] *Ber.*, **22**, 1009 (1889).

[2] *Loc. cit.*

fourths of this nitrogen is liberated by hypochlorous acid. The remaining nitrogen atom is no doubt held in solution as cyanide or cyanate. An experiment carried out with potassium cyanide and sodium hypochlorite solution failed to give any nitrogen. It may be said that Pohl's experiments were carried out with too great a dilution of hypochlorite and consequently the evolution of nitrogen was exceedingly slow and never completed.

The Action of Nitrous Acid upon Dicyanodiamide.—The apparatus devised by Van Slyke[1] was found unacceptable as no nitrogen whatsoever could be obtained even after the operation had continued for an hour or more. In order to bring about the conditions which we deemed essential for the interaction of nitrous acid and dicyanodiamide, substantial changes were required in the construction of the apparatus. A small flask (50 cc.) is fitted with a 3-hole rubber stopper. Through one of these holes an inlet tube, admitting a stream of pure dry carbon dioxide, is made to extend almost to the bottom of the flask. Through the second hole a small glass rod is made to slip easily. The lower end of the rod is slightly bent and may be dropped almost to the bottom of the flask. Through the third hole extends an outlet tube for gas and vapor; this tube leads through a very short cold water condenser jacket (placed close to the flask itself so that the vapors from the boiling mixture are quickly condensed and returned to the flask) and then directly into a series of 3 wash bottles each containing about 60 cc. of alkaline permanganate solution (50 g. potassium permanganate and 25 g. potassium hydroxide per liter of solution), and finally into an azotometer containing a 50% potassium hydroxide solution. The nitric oxide liberated by the reaction in the flask is, for the most part, absorbed by the permanganate solution. In order that the last traces of the oxide may be removed the gas collected in the azotometer is transferred, just as described by Van Slyke, to a Hempel pipet containing alkaline permanganate and well shaken. After this operation the gas is returned to the azotometer and finally to the eudiometer tube for measurement of volume over water. The dicyanodiamide is carefully weighed and admitted to the flask along with the acid (about 25 cc.). About 2 g. of pure sodium nitrite (in stick form) is now placed in a 4 cm. test tube. The bent end of the glass rod is then inserted in the mouth of the test tube and the two together lowered into the flask during the operation of closing the latter. The test tube is easily maintained in an upright position, and its contents thus kept free of the acid mixture, by allowing the bent end of the glass rod to press the test tube firmly against the inlet tube supplying the carbon dioxide.

When the apparatus is thus arranged, a stream of carbon dioxide is admitted until all of the air in the train of vessels is displaced. The

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[1] *Loc. cit.*

stream of gas is then checked and the reaction mixture brought almost to boiling. The glass rod which supports the small test tube of sodium nitrite is finally raised and the salt thereby allowed to come in contact with the acid. The reaction usually requires 12 to 15 minutes after which carbon dioxide is again admitted to the apparatus and all of the nitrogen swept out into the azotometer. Any nitric oxide which may still be mixed with the nitrogen is readily removed by means of the Hempel pipet previously mentioned. The following table displays the results obtained in the reaction of nitrous acid upon (A) dicyanodiamide itself; upon (B) the condensation product prepared according to Pohl[1] by allowing an aqueous solution of formaldehyde and dicyanodiamide to evaporate spontaneously; and upon (C) guanidine carbonate, the last given only by way of comparison between the method here and that used by Van Slyke[1] where the nitrogen liberated is *nil.* From a number of blank determinations made in the same length of time (12–15 minutes) but without the amino derivative, the average volume of unabsorbed gas amounted to 1.4 cc. The volume of nitrogen collected in each experiment has accordingly been reduced by this amount (1.4 cc.) before the record was set down in the table.

TABLE I.—REACTIONS WITH NITROUS ACID.

Wt. sample.	Conc. of hot acid.	Vol. N_2 over H_2O. Cc.	Temp. Degrees.	Corr. press. Mm.	Vol. N_2 0°, 760 mm. Cc.	Theory for Cc.
	A. Dicyanodiamide + Nitrous Acid.					
0.0793	50% acetic	6.8	24	730	5.82	1N = 21.15
0.0567	50% acetic	7.0	24	745	6.1	1N = 15.11
0.0625	70% acetic	11.6	21	748	10.34	1N = 16.67
0.0885	80% acetic	20.8	22	748	18.45	1N = 23.59
0.0762	85% acetic	24.1	24	740	20.92	1N = 20.32
0.0458	85% acetic	14.6	18	747	13.20	1N = 12.22
0.0536	85% acetic	16.8	19	746	15.08	1N = 14.3
0.0484	90% acetic	18.2	24	745	15.92	1N = 12.91
0.0684	95% acetic	32.0	24	748	28.1	2N = 36.48
0.0462	Glacial acetic	44.3	20	746	39.6	3N = 36.95
0.0526	Glacial acetic	42.8	18	740	38.3	3N = 42.09
0.0528	Glacial acetic	42.6	20	746	38.1	3N = 42.23
0.0568	85% Phosphoric	71.2	23	735	61.7	4N = 60.57
	B. Formaldehyde-Dicyanodiamide + Nitrous Acid.					
0.0712	Glacial acetic	43.1	19	740	38.37	3N = 43.2
0.0826	85% acetic	2.2	21	742	1.9	1N = 16.5
0.0914	85% acetic	1.7	22	745	1.5	1N = 18.3
	C. Guanidine Carbonate + Nitrous Acid.					
0.0950	50% acetic	5.6	22	729	4.84	2N = 59.6
0.0486	85% acetic	4.0	23	634	3.5	2N = 24.19
0.0730	Glacial acetic	40.4	22	734	35.15	2N = 36.35
0.0481	80% glacial acetic and 20% isobutyric	26.6	23	734	23.02	2N = 23.94

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[1] *Loc. cit.*

1-Cyano-2-imino-4,6-dimethyl-1,2-dihydropyrimidine, $C_4HN_2(.CN)(:NH)(CH_3)_2$ (XVI).—Two g. of dicyanodiamide was dissolved in 25 cc. of water and 3.3 g. (1.25 mol.) acetylacetone added. About 20 drops of 2 *N* sodium hydroxide solution were added as condensing agent. The mixture was placed in a flask provided with reflux condenser and heated 24 hours on a water bath. From the final yellow solution, upon cooling, there separated fine, colorless needles of the condensation product. The crystalline mass was washed with alcohol and purified by recrystallization from alcohol. The yield was 1.8 g. or 50% of the theoretical. Imino-cyanodimethylpyrimidine is fairly soluble in water, alcohol, acetone, chloroform or ethyl acetate; slightly soluble in ether or benzene; and insoluble in carbon tetrachloride, carbon disulfide or ligroin. The pure product melts at 225°. This compound may also be prepared from dicyanodiamide and acetylacetone, without the aid of a condensing agent, if an aqueous solution of the two is boiled for many hours. The yield, however, is very poor. Piperidine and sodium hydroxide were found to be the best condensing agents but these are not productive of good results unless the reaction mixture is kept in the neighborhood of 100°. Acids were found inaffective whether employed in aqueous or alcoholic solutions of the mixed compounds.

Calc. for $C_7H_8N_4$: C, 56.71; H, 5.44; N, 37.84. Found: C, 56.79; H, 5.60; N, 37.69.

Silver Salt of Imino-cyanopyrimidine, $C_7H_7N_4Ag$.—When an aqueous solution of the iminocyanopyrimidine was treated with a silver nitrate solution a white, curdy precipitate of the monoargentic salt was precipitated. After thorough washing with water the compound was dried and analyzed. The results indicate that one hydrogen atom in the condensation product (naturally the imino hydrogen) is replaced by metal.

Calc. for $C_7H_7N_4Ag$: Ag, 42.34. Found: Ag, 41.69.

2-Imino-4,6-dimethyl-1,2-dihydropyrimidine, $C_4H_2N_2(:NH)(CH_3)_2.H_2O$ (XIX).—One g. of the pure imino cyanopyrimidine was dissolved in 25 cc. of dil. (1 : 5) sulfuric acid and the solution boiled under a reflux condenser for 3 hours. The final yellow solution was then diluted to a volume of 200 cc., neutralized with moist freshly precipitated barium hydroxide and filtered. The clear filtrate was evaporated to dryness upon a water bath and the yellow residue taken up in a small quantity of absolute alcohol from which, upon cooling, the lemon yellow prisms soon separate. The yield was approximately 70% of the theoretical. The same compound may also be prepared by 3 hours' boiling of the imino cyanopyrimidine in conc. hydrochloric acid, or 1 hour's heating of this same solution in sealed tube at 125°. The reaction mixture is evaporated directly to dryness, taken up in water, just neutralized with potassium hydroxide, again evaporated to dryness and extracted with absolute alcohol. The final product in either case is purified by recrystallization from alcohol. The anhydrous light yellow imino-methylpyrimidine melts, with decomposition, at 199°. The vapors of ammonia are easily recognizable in the decomposition products. This compound is readily soluble in water; fairly soluble in alcohol or acetone; slightly soluble in ethylacetate, chloroform, or benzene; and insoluble in ether or ligroin. As crystallized from alcohol it contains one molecule of water of hydration. This water may be removed completely by careful drying for one hour at 130°.

Calc. for $C_6H_9N_3.H_2O$: C, 51.04; H, 7.85; N, 29.78; H_2O, 12.75. Found: C, 51.34; H, 7.98; N, 29.71; H_2O, 12.94.

The amino-dimethyl pyrimidine (XI) was prepared in accordance with the method of Combes[1] by warming a mixture of guanidine and acetylacetone. The colorless product crystallizing out of the reaction mixture is practically pure. It is readily soluble in alcohol or ethylacetate; fairly soluble in water, benzene, acetone or chloroform; and slightly soluble in ether or ligroin. It melts at 153°. The evolution of ammonia, however, can not be detected till a considerable overheating, and consequent decomposition, has taken place. The properties of this aminopyrimidine are thus seen to be widely variant from those of the iminopyrimidine previously described.

Action of Alkali upon the Imino-dimethylpyrimidine.—One g. of the pure 2-imino-4,6-dimethyldihydropyrimidine was dissolved in 20 cc. of 4 *N* sodium hydroxide solution and the mixture heated under a reflux for 3 hours. The final solution was carefully neutralized with hydrochloric acid and evaporated to dryness upon a water bath. The dry residue was extracted with absolute alcohol and the alcoholic solution again evaporated to dryness. The final residue was then dissolved in water, boiled with animal charcoal, filtered and finally evaporated to a small volume over a water bath, whereupon after cooling small lemon-yellow crystals appeared. These crystals contained 2 molecules of water of hydration which may be completely removed by drying over sulfuric acid. The anhydrous substance is readily soluble in chloroform; fairly soluble in alcohol, water, acetone, benzene or ethyl acetate; and insoluble in ether or ligroin; m. p. 197°. This melting point and the general characteristics indicate acetylacetoneurea; the solubilities just given check with the solubilities of pure anhydrous acetylacetoneurea as prepared by us. No odor of ammonia can be detected from the melted product, hence we may conclude that the action of the strong alkali removed the imino group from the iminodimethylpyrimidine. The complete analysis of this final product, as given below, confirms in every way its identification as acetylacetoneurea (XX).

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[1] *Loc. cit.*

Calc. for $C_6H_8N_2O$: C, 58.05; H, 6.49; N, 22.58. Found: C, 58.64; H, 6.70; N, 22.43.
Calc. for $C_6H_8N_2O.H_2O$: H_2O, 22.51. Found: H_2O, 22.80.

Action of Alkali upon Cyano-iminodimethylpyrimidine.—The action of acids upon this compound results in the saponification of the cyano group. The action of alkali upon the final product has just been shown to give acetylacetoneurea. It was hoped therefore that this latter step, the elimination of the imino group, could be accomplished first by the action of alkali upon the original condensation product. One g. of this cyano-iminopyrimidine was boiled with 6 *N* sodium hydroxide solution for 6 hours. The mixture was neutralized with hydrochloric acid, evaporated to dryness over a water bath and extracted with alcohol. The colorless product finally obtained melted at 218° and consisted of a mixture of the original substance and a cyanodimethylpyrimidine. This latter could not be isolated from the mixture, but its presence there was demonstrated by treating the mixture with dil. (1 : 5) sulfuric acid as described under the preparation of iminopyrimidine. From the final dry residue acetylacetoneurea in small amount could easily be extracted by chloroform. Acetylacetoneurea can not be obtained by the action of acids upon the original condensation product but by the action of alkali upon the residue from the acid saponification it is easily prepared. It is reasonable to suppose therefore that to a very small extent the action of alkali upon the condensation product may lead directly to a cyanopyrimidine through the elimination of the imino group. As the results here were unsatisfactory, the direct condensation of acetylacetone with cyanurea, as well as biuret, was attempted.

Condensation of Cyanurea with Acetylacetone.—Cyanurea was prepared according to the directions of Hallwachs[1] wherein dicyanodiamide is decomposed by a barium hydroxide solution. To 1 g. of cyanurea and 2 g. of acetylacetone, dissolved in 40 cc. absolute alcohol, 15–20 drops of conc. sulfuric acid was added and the solution set aside. After several days, crystals of a sulfate had collected. These crystals were dissolved in water and the solution neutralized with freshly precipitated barium carbonate. From the clear filtrate, upon evaporation, the characteristic yellow prisms of acetylacetoneurea soon made their appearance. Hydrochloric acid is equally effective in this condensation; both of these acids readily saponify the cyano group and consequently acetylacetoneurea is the only result possible. The use of sodium hydroxide and also piperidine failed to bring about the condensation desired. Reactions attempted at higher temperatures in alcohol or in aqueous solutions, with or without alkaline condensing agents, gave only negative results.

Condensation of Biuret with Acetylacetone.—The biuret was prepared from cyanurea according to the method of Baumann.[2] To 1 g. of biuret

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[1] *Ann.*, **153**, 295 (1870).

[2] *Ber.*, **8**, 708 (1875).

and 2 g. of acetylacetone, dissolved in 40 cc. absolute alcohol, 15–20 drops of conc. sulfuric acid was added and the solution set aside. After several days crystals of a sulfate separated. These crystals were dissolved in water and the solution treated as described in preceding paragraph. The result is again acetylacetoneurea. Alkalies fail to bring about any condensation whatsoever. The action of acids however favors a saponification here of the amido group just as also of the cyano group in cyanurea. The end result in both cases must be urea and consequently in this condensation, an acetylacetoneurea.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE IDENTIFICATION OF THE CINCHONA ALKALOIDS BY OPTICAL-CRYSTALLOGRAPHIC MEASUREMENTS.[1]

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Optical crystallographic methods of identification of crystallized substances have been in recent years of great service in mineralogy and geology, and it has been repeatedly suggested that they should also be useful in connection with synthetic compounds.[2] The senior author has recently applied these methods to some of the problems encountered by the food and drug analyst. The present paper represents the following up of one of the subjects outlined by Dr. Wright.[3]

It was decided first to ascertain the value of these methods in the distinction of alkaloids which occur together or are difficult to recognize by chemical means. Samples of the 4 cinchona alkaloids were purchased on the open market and submitted to purification and recrystallization. This work was carried on by the junior author, who has supplied the chemical data given in the tables. The optical properties were then measured under the microscope by the senior author. As these substances are soluble in the mixtures of oils usually employed for the immersion method of determining refractive indices, solutions of known indices prepared from potassium-mercuric iodide and glycerol were used. The data for each alkaloid are presented first in a standard formal description, and then in tabular form to bring out the differences between them; determinative tables which may be followed in practice are included. The results obtained in the study of mixtures and of a proprietary

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[1] Presented in abstract form at the November, 1917, meeting of the Association of Official Agricultural Chemists.

[2] Compare William H. Fry, "Identification of Commercial Fertilizer Materials," U. S. Dept. Agr., *Bull.* **97**, 13 pp. (1914); Fred E. Wright, "The Petrographic Microscope in Analysis," THIS JOURNAL, **38**, 1647 (1916); Emile M. Chamot, "Chemical Microscopy," *J. Ind. Eng. Chem.*, **10**, 60 (1916).

[3] *Loc. cit.*