

V. *Researches regarding the Molecular Constitution of the Volatile Organic Bases.*

*By Dr. A. W. HOFMANN, F.C.S., Professor of the Royal College of Chemistry of London. Communicated by Sir JAMES CLARK, Bart., F.R.S.*

Received December 26, 1849,—Read January 17, 1850.

THE limited number of elementary substances which are concerned in the elaboration of the endless variety of organic compounds, long ago directed the course of chemical inquiry into the channel of speculations as to the mode in which the various constituents are grouped in bodies of this nature. The necessity of these speculations became more and more imperative as the boundary of the science extended; they were indeed forced upon us by the discovery of substances isomeric with each other which deprived us of the resort to mere quantity for the explanation of their contrasting qualities. Wild and incongruous though some of the views, proposed from time to time, may have been, it must be admitted that their influence upon the progress of chemistry has been most beneficial; especially in the organic department of this science, it is to the theory of the compound radicals, the result of these speculations, that we are indebted for the light which now begins to dawn upon the chaos of collected facts, even if we should never succeed in isolating these radicals.

Among the various classes of organic substances, there is perhaps none of which, from an early period, chemists have so constantly endeavoured to attain a general conception as the group of compounds which have received the name of organic bases, all—and they are now very numerous—being capable of combining, like the metallic oxides, with acids, and being derived either from vital processes in animals or plants, or from a variety of artificial reactions conducted in the laboratory.

The remarkable analogy between all these substances and ammonia, which in its turn imitates as it were in its chemical deportment the mineral oxides, naturally attracted the notice of chemists soon after SERTÜNER's discovery of the first of these alkaloids in the beginning of this century. Nor have they ever since been classified separately from ammonia; philosophers have only differed as to the mode of their relation with the typical compound.

Of the theories which have been enunciated respecting the constitution of the organic bases, there are two of chief importance, which may be designated as the ammonia- and the amidogen-theory, the former having been first proposed by BERZELIUS\*, while the latter we owe to LIEBIG†. According to the former of the two

\* *Traité de Chimie*, vi. p. ii.

† *Handwörterbuch der Chemie* von LIEBIG, WÖHLER und POGGENDORFF, Bd. i. p. 699. Artikel Organische Basen.

chemists, the ammonia would pre-exist in the organic bases; these bodies would be conjugated compounds of ammonia with various adjuncts, containing either carbon and hydrogen, or these elements together with nitrogen, oxygen and even sulphur, compounds in which the original character of the ammonia has only been slightly modified by the accession of the adjunct. This view is chiefly supported by the mode and the proportions in which these alkaloids combine with acids, and by the fact, that various organic substances, by directly uniting with ammonia, give rise to the formation of basic compounds which are perfectly analogous to the alkaloids occurring in the economy of nature. According to LIEBIG's opinion, ammonia would no longer exist in the organic bases. At the time when LIEBIG\* wrote upon this subject, the attention of chemists was much engaged with the study of a class of compounds, known under the name of amides, the prototype of which, oxamide, was discovered by DUMAS. These substances, all strictly neutral, originate from ammonia by the loss of one equivalent of hydrogen, which is abstracted by the oxygen or chlorine of certain electro-negative bodies (as in the formation of oxamide and benzamide), a hypothetical substance, amidogen,  $\text{H}_2\text{N}$ , remaining in combination with the oxide or chloride, deprived of 1 equiv. of oxygen or chlorine. LIEBIG thought that the formation of the organic bases might take place in a similar manner, namely, by a reduction of ammonia to the state of amidogen, by the action of electro-positive organic oxides.

Each of these theories being expressed in a simple formula, the organic bases, according to BERZELIUS, would be represented by the terms



while LIEBIG's view would characterize them as



X denoting generally an organic compound containing carbon, hydrogen, and possibly nitrogen, oxygen and sulphur, while Y expresses an organic oxide, chloride, &c., *minus* 1 equiv. of oxygen, chlorine, &c.

Objections have been raised against either theory, and the opinions of chemists have remained divided. LIEBIG has not returned any more to the subject, but BERZELIUS took frequent occasion, both in his 'Annual Report' and in the several editions of his 'Traité,' to defend his notion by the skilful interpretation of every new fact which was elaborated by the progress of the science. The weight of his authority has not been without influence, for it cannot be denied that BERZELIUS's view has become more and more generally accepted, especially since a series of comparative researches, conducted of late upon the derivatives of the salts of ammonia and of organic bases, appeared to give fresh support to this theory. These experiments pointed out that the elimination of hydrogen from organic bases and ammonia is by no means confined to one equivalent; oxalate of ammonia, which by the loss of 2 equivs. of water is converted into oxamide, when deprived of the whole of its hydrogen in

\* *Loc. cit.* p. 235.

the form of water, becomes cyanogen (oxalonitrile); an analogous change occurs with the acid salts of ammonia, resulting in the formation of two classes of compounds, differing, the one by two, the other by four equivalents of water, from the original salt.

The representation of several of these groups in analogous derivatives from the salts of organic bases, especially from the salts of aniline, could not but strengthen the belief that ammonia actually pre-exists in the organic alkaloids. Incidentally to some researches communicated to the Chemical Society of London\*, I gave a synopsis of all the facts supporting the view of BERZELIUS.

The prosecution however of this inquiry has elicited many points, which are scarcely reconcileable with this theory. In another paper† I endeavoured to show that the force of the argument in favour of this view, derived from the considerations just stated, is greatly neutralized on the completion of the comparison between the two series by the failure of the analogy, just at the point where its occurrence would have been most decisive. Now this very failure is not only in perfect harmony with, but would be required by, the theory of amidogen-bases.

Yet stronger grounds for the acceptance of the latter view have been afforded by a splendid investigation of M. WURTZ‡ on the compounds of ethers with cyanic acid, which have actually realized a series of substances, anticipated in a most remarkable manner by LIEBIG on the theoretical ground of his conception of the nature of these compounds. Instances of such anticipation of discovery are so rare, that I may be allowed to quote the words in which LIEBIG predicted nearly ten years ago the discovery of M. WURTZ:—"If," said LIEBIG§, in continuing the development of his ideas respecting the constitution of the organic bases, "we were enabled to replace by amidogen the oxygen in the oxides of methyl and ethyl, in the oxides of two basic radicals, we should without the slightest doubt obtain a series of compounds exhibiting a deportment similar in every respect to that of ammonia. Expressed in symbols, a compound of the formula



would be endowed with basic properties."

Now these compounds, imagined in 1840 by LIEBIG in illustration of his views, have sprung into existence in 1849, with all the properties assigned to them by that chemist. At the beginning of the present year, M. WURTZ, in investigating the cyanates of ethyl, methyl and amyl, arrived at the unexpected result that these compounds, when decomposed by potassa, undergo a change analogous to that of cyanic acid. This acid, when treated with potassa, yielding carbonic acid and ammonia, the corresponding ethers were split into carbonic acid and compound ammonias of the exact formula indicated in LIEBIG's suggestion.

It would be difficult to imagine a more brilliant triumph for any theoretical specu-

\* Researches on the Volatile Organic Bases, III. Action of Chloride, Bromide and Iodide of Cyanogen upon Aniline, Chem. Soc. Quart. Journ. i. p. 285.

† Chem. Soc. Quart. Journ. ii. p. 331.

‡ Compt. Rend. xxviii. p. 223.

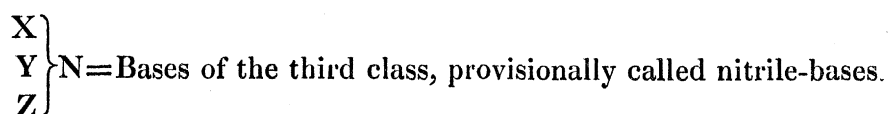
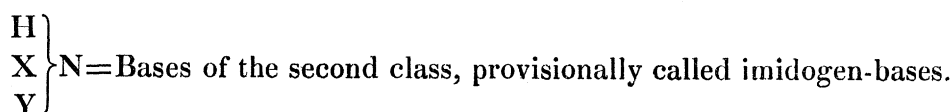
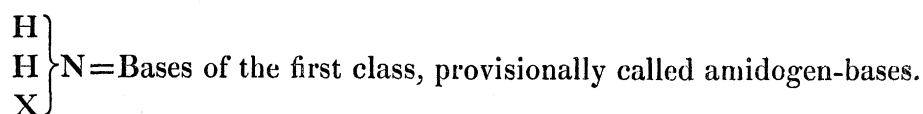
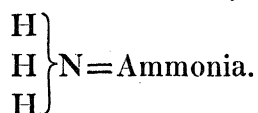
§ *Loc. cit.* p. 235.

lation ; I have however no doubt that even the illustrious propounder of this view is at present far from believing that all the organic bases are amidogen-compounds. The progress of our knowledge has changed the form of this view, without shaking its foundation. A good theory is more than a *temporary* expression of the state of science, collecting under a general view the facts acquired up to the moment of its birth. It will not, like ephemeral hypothesis, vanish before the light of succeeding discoveries, but expanding with the growth of science, it will still correctly represent the known facts, though of necessity modified into a more general expression.

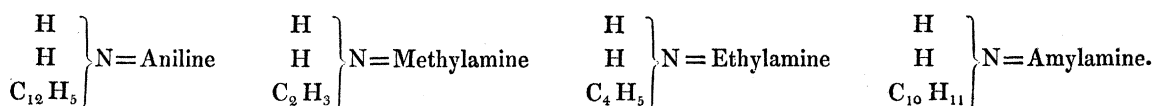
Such a theory then was that of LIEBIG. Resting as it did, upon the facts observed in the formation of the neutral amides, it was, as originally framed, an expression of the knowledge we then possessed. Subsequent researches showed that it was not only the 1 equiv. of hydrogen (the abstraction and replacement of which had led us to amidogen and the amides) that could be removed from the ammonia, but that similarly 2 equivs., and even the whole of the hydrogen could be withdrawn from their position in this base and substituted by other atoms, as in the imides and nitriles.

If then we give to LIEBIG'S view the extension of which it naturally admits, and which is demanded by the onward steps of science, we arrive at a more general conception of the nature of the organic bases ; amidogen and the amides now presenting themselves to us only as particular instances of the permutations possible among the elements of the primary type ammonia. It seemed but logical to look among the bases for analogues too of the imidogen-compounds and the nitriles. In other words, it appeared desirable to inquire whether the several equivalents of hydrogen in ammonia could not be replaced, not only by atoms neutralizing the basic properties of the original system, but also by elements or groups of elements, not affecting, or but slightly modifying the alkaline character of the primary compound. Were this possible, we should arrive at the formation of three classes of organic bases, derived from ammonia by the replacement respectively of 1, 2 or 3 equivalents of hydrogen.

Expressed in formulæ, these compounds would be—



The bases belonging to the first class are pretty numerous represented. Aniline, methylamine, ethylamine, amylamine, when considered as amidogen-compounds, belong to this group.



Bases of the second and third of the above classes had not been hitherto obtained, although it is not improbable that many of the alkaloids, whose constitution is at present perfectly unknown, may be found on a closer investigation to be members of these latter groups.

The researches which I have the honour of presenting to the Royal Society will exhibit a series of artificial bases, which are evidently produced, by the substitution of carbohydrides, for the second and third equivalents of hydrogen in the ammonia.

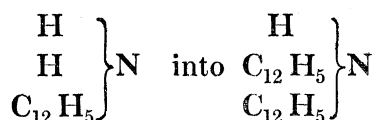
Before proceeding however to the details of my experiments, I shall state, that I am far from supposing that the above formulæ include the constitution of all the complex bases with which we are acquainted. It is chiefly the volatile alkaloids whose constitution may be represented by this view, but even here exceptions may occur.

Both the ammonia- and the amidogen-theory of the organic bases appear to me to have the same defect, in that they endeavour to compress into a single proposition our notions respecting the endless variety of compounds which are united under the collective term organic bases. If we reflect upon the manifold sources from which the various groups of alkaloids are derived and the differences which we observe in their physical properties, and even in their chemical deportment, it is but natural to assume that in their constitution a diversity may exist similar to that of the organic acids, which we cannot attempt to include under one common theory of construction. On comparing the alkaloids of the Cinchona bark with urea and creatinine, or with nicotine and aniline, few chemists indeed will be inclined to believe that the constituents in these various substances are arranged in the same manner. The constitution of the non-volatile organic bases will probably present a very considerable diversity; and it is not at all unlikely that this class will exhibit even instances of conjugated ammonias in BERZELIUS's acceptance of the term.

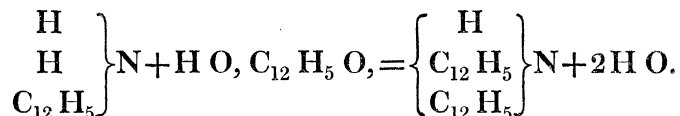
In commencing my experimental inquiry, the first step was to select the particular base which should be the subject of operation, and the radicals whose introduction should be attempted. On the one hand, my previous experimental occupations suggested aniline for the foundation; while, on the other, the radicals existing in aniline and its congeners, methylamine, ethylamine and amylamine, namely, phenyl, methyl, ethyl and amyl, presented themselves as materials for construction.

#### ACTION OF PHENYL-ALCOHOL ON ANILINE.

My endeavours to introduce into aniline a second equivalent of phenyl, in order to convert



have been unsuccessful up to the present moment. I had hoped that this conversion might be effected by the action of phenyl-alcohol on aniline according to the following equation:—



Phenyl-alcohol, however, has neither at the common nor at a high temperature—the mixture was exposed for several days in a sealed tube to 250° in an oil-bath—any action upon aniline. The residuary aniline was identified by analysis. When converted into a platinum-salt—

0·3120 grm. of the salt left on ignition 0·1024 grm. of platinum.

Experimental percentage of platinum.  
32·82

Theoretical percentage in the aniline-platinum-salt.  
32·98

This experiment, when repeated for a longer period, might possibly give a more satisfactory result. It is known that ammonia, by a similar treatment with phenyl-alcohol, is likewise only very slowly converted into aniline.

The action of chloride and bromide of phenyl  $\text{C}_{12}\text{H}_5\text{Cl}$ , and  $\text{C}_{12}\text{H}_5\text{Br}$  upon aniline promised a better result; but the difficulties which I encountered in preparing these compounds, which are as yet but very imperfectly investigated, deterred me from farther pursuing this direction of the inquiry.

Much more successful were my endeavours to substitute methyl, ethyl and amyl for the remainder of the basic hydrogen in aniline. The compounds of these radicals with chlorine, bromine and iodine appeared to be the most appropriate substances for this purpose. I have worked with these three classes of compounds, but finding that the use of the chlorides and iodides is attended with inconveniences, the former compounds being exceedingly difficult to handle on account of their volatility, while the latter often complicate the reactions by the rapid decomposition of the hydriodic acid formed in the process, I have almost exclusively employed the bromides, whose action is so precise and definite as to preclude the necessity of seeking any farther agent; only when working in the methyl-series I have sometimes preferred to employ the iodide, which is far less volatile than the bromide. Still the deportment of the iodides presents some peculiarities, which require farther elucidation.

#### ACTION OF BROMIDE OF ETHYL UPON ANILINE.

On adding dry bromide of ethyl to aniline, no change takes place in the cold, but on gently heating the mixture in an apparatus which will allow the volatilized bromide to return to the aniline, a lively reaction ensues. The liquid remains for some time in a state of ebullition, and solidifies on cooling into a mass of crystals. If a

cold mixture of the two bodies be left for a few hours, it deposits crystals, which are much more definite than those obtained on the cooling of the hot solution. In either case the fluid assumes a deep amber colour which approaches brown, and the crystals are usually slightly yellow. These crystals vary in composition according to the proportions in which the two bodies have been mixed. If a very large excess of aniline has been used, they are of a prismatic character, and consist of pure hydrobromate of aniline. This compound was identified by analysis:—

0·0486 grm. of the crystals gave 0·0525 grm. of bromide of silver.

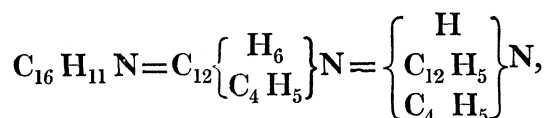
Experimental percentage of bromine.

45·88

Theoretical percentage of bromine in  
hydrobromate of aniline.

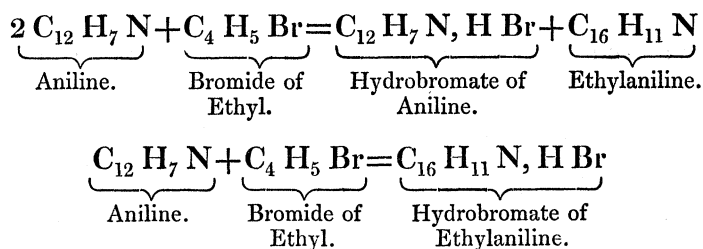
45·97

On the other hand, if the bromide of ethyl predominates to a considerable extent, the crystals are flat, four-sided tables, sometimes of considerable size. Several analyses, the details of which will be found below, showed that they were the hydrobromate of a new base\*, represented by the formula—



*i. e.* of aniline in which 1 equiv. of hydrogen is replaced by 1 equiv. of ethyl, or ammonia in which 2 equivs. of hydrogen are replaced, the one by phenyl, the other by ethyl. The same base is contained in the free state, either alone or mixed with aniline in the mother-liquor of the crystals of hydrobromate of aniline, while the mother-liquor of the hydrobromate of the new base, especially if a large excess of the bromide has been employed, and after some days' standing, consists of nearly perfectly pure bromide of ethyl, only a small quantity of the hydrobromate in question being kept in solution.

The formation of the new basic compound, for which I propose the name Ethyl-aniline or Ethylophenylamine, takes place by the removal, from aniline, of 1 equiv. of hydrogen, in the form of hydrobromic acid, for which an equivalent of ethyl is substituted, the compound thus produced uniting with the hydrobromic acid. Hence the action of bromide of ethyl upon aniline may be represented by the following two simple equations:—



\* Frequently, as may be imagined, mixtures of the two hydrobromates are deposited according to the proportion in which the constituents are mixed.

*Ethylaniline (Ethylophenylamine).*

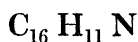
This base may be readily obtained in a state of purity by decomposing the solution of the hydrobromate with a concentrated solution of potassa. A brown basic oil rises at once to the top of the liquid; it is separated by means of a pipette or a tap-funnel, and subjected to rectification, after having been freed from water by standing over solid potassa. Thus a colourless transparent oil is obtained, which rapidly turns brown on exposure to air and light, and has a very high refractive power. It has all the properties of the oily bases in general. From aniline it is distinguished by a slight difference in the odour, perhaps imperceptible to an inexperienced nose, by a higher boiling-point and a lower specific gravity. Ethylaniline boils (from platinum) constantly at  $204^{\circ}$ , the boiling-point of aniline being  $182^{\circ}$ ; the specific gravity of this base is 0.954 at  $18^{\circ}$ , that of aniline being 1.020 at  $16^{\circ}$ . Ethylaniline does not exhibit the violet coloration with chloride of lime which characterizes aniline. Its acid solutions impart a yellow colour to fir-wood and the pith of elder-tree, although less intensely than those of aniline. By dry chromic acid the base is inflamed like aniline.

Analyses performed with protoxide of copper gave the following results:—

- I. 0.2566 grm. of oil gave 0.7470 grm. of carbonic acid\*.  
 II. 0.3048 grm. of oil gave 0.8850 grm. of carbonic acid, and 0.2544 grm. of water.

	Percentage-composition.	
	I.	II.
Carbon . . . .	79.39	79.19
Hydrogen . . . .	—	9.27

The formula



requires the following values:—

	Theory.		Mean of experiments.
16 equivs. of Carbon . . . . .	96	79.33	79.28
11 equivs. of Hydrogen . . . . .	11	9.09	9.27
1 equiv. of Nitrogen . . . . .	14	11.58	—
1 equiv. of Ethylaniline . . . . .	121	100.00	

The salts of ethylaniline are remarkable for their solubility, especially in water. They are not easily obtained in well-defined crystals from an aqueous solution. From alcohol, in which they are somewhat less soluble than in water, several salts may be readily crystallized. Both the hydrochlorate and oxalate are obtained only on evaporating their solutions nearly to dryness, when the salts separate in the form of radiated masses; the sulphate and nitrate have not as yet been obtained in the solid form.

\* The hydrogen was lost.



*Hydrobromate of Ethylaniline.*

The hydrobromate is extremely soluble in water, but crystallizes on spontaneous evaporation of its alcoholic solution in splendid regularly formed tables, of considerable size and perfect beauty. I intend to give the measurement of these crystals in a future communication. The analyses of this salt, dried at 100°, gave the following results:—

- I. 0·6412 grm. of hydrobromate gave 0·5956 grm. of bromide of silver.  
 II. 0·5553 grm. of hydrobromate gave 0·5216 grm. of bromide of silver.

Percentage of Hydrobromic Acid.	
I.	II.
40·01	40·47

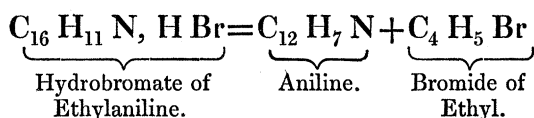
The formula



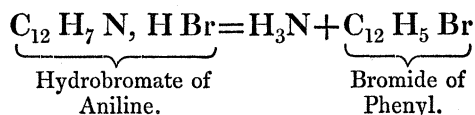
requires the following values:—

	Theory.		Mean of experiment.
1 equiv. of Ethylaniline . . . . .	121	59·91	—
1 equiv. of Hydrobromic Acid . . . . .	81	40·09	40·24
1 equiv. of Hydrobromate of Ethylaniline	202	100·00	

The hydrobromate of ethylaniline when gently heated sublimes, like the corresponding aniline-salt, in splendid needles, but when subjected to the action of a rapidly increasing heat it undergoes a very remarkable decomposition, being re-decomposed into aniline and bromide of ethyl. On addition of hydrochloric acid to the distillate, the aniline dissolves, while the bromide of ethyl collects as a heavy oil at the bottom of the vessel.



I have in vain tried to split hydrobromate of aniline according to the equation



This salt sublimes, even when suddenly heated, without any decomposition.

*Platinum-Salt of Ethylaniline.*

I have controled the formula of ethylaniline moreover by the analysis of the platinum double salt of this substance. This salt is likewise very soluble, and may by this property be distinguished from the corresponding aniline-salt; on addition of a concentrated solution of bichloride of platinum to a concentrated solution of this

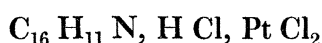
hydrochlorate, a deep orange-red oil is deposited, which solidifies, sometimes only after half a day, with crystalline texture. If a moderately concentrated solution be employed, the salt crystallizes in the course of a few hours in magnificent yellow needles, often of an inch in length. On account of its great solubility in water and alcohol, it has to be washed with a mixture of alcohol and ether, in which the latter predominates. It may be dried at  $100^{\circ}$  without decomposition.

On analysis the following numbers were obtained :—

0.3550 grm. of platinum-salt gave 0.3275 grm. of carbonic acid and 0.1055 grm. of water.

0.1812 grm. of platinum-salt gave 0.0545 grm. of platinum.

The formula



requires the following values :—

	Theory.		Experiment.
16 equivs. of Carbon . . . . .	96.00	29.34	29.24
12 equivs. of Hydrogen . . . . .	12.00	3.66	3.83
1 equiv. of Nitrogen . . . . .	14.00	4.29	—
3 equivs. of Chlorine . . . . .	106.50	32.55	—
1 equiv. of Platinum . . . . .	98.68	30.16	30.07
1 equiv. of Platinum-salt . . . . .	326.18	100.00	

Terchloride of gold and protochloride of mercury yield with solutions of ethylaniline yellow oily precipitates, which are very readily decomposed.

Of the products of decomposition of ethylaniline, I know as yet almost nothing, although they will not be deficient in interest in a theoretical point of view.

The action of bromine gives rise to the formation of two compounds, both crystalline, one basic, the other indifferent and corresponding probably to tribromaniline. Neither of these substances has yet been analysed.

On passing cyanogen into an alcoholic solution of ethylaniline, short yellow prisms are deposited after some time, which are evidently cyanethylaniline, Cy,  $\text{C}_{16} \text{H}_{11} \text{N}$ , corresponding to cyaniline and cyanocumidine\*. This new cyanogen-base dissolves in dilute sulphuric acid, and is thrown down from this solution by ammonia in form of a floury precipitate. The hydrochlorate, like the corresponding cyaniline-salt, is very insoluble in hydrochloric acid. It may be obtained in fine crystals on addition of hydrochloric acid to a solution of the base in dilute sulphuric acid. Cyanethylaniline, like cyaniline, forms a very soluble platinum-salt.

I have made also some qualitative experiments respecting the deportment of ethylaniline with chloride of cyanogen. This gas is rapidly absorbed, much heat being evolved. On cooling, the mass solidifies into a resinous mixture of a hydrochlorate and a neutral oil, which separates on addition of water. The base separated from

\* Chemical Society, Quart. Journ. i. p. 159.

the hydrochlorate is an oil, and volatile, while melaniline, produced in the corresponding reaction of chloride of cyanogen with aniline, is solid and non-volatile.

Bisulphide of carbon gives rise to a gradual evolution of hydrosulphuric acid, no crystals being deposited from the mixture.

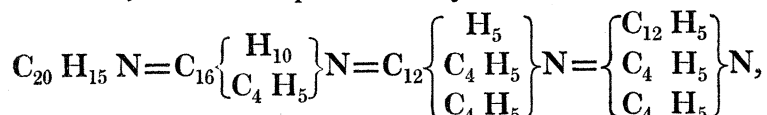
Phosgene gas acts powerfully on ethylaniline, a liquid compound being formed together with hydrochlorate of ethylaniline. No analysis having as yet been performed of these compounds, I refrain from entering into any farther details.

#### ACTION OF BROMIDE OF ETHYL UPON ETHYLANILINE.

The phenomena attending the action of bromide of ethyl upon ethylaniline resemble those which are observed in the corresponding treatment of aniline. The reaction however is less powerful, another equivalent of hydrogen in aniline being less easily eliminated or replaced. Four or five days elapse before the separation of crystals commences at the common temperatures. The formation however is considerably accelerated on application of heat.

The experience obtained in the preparation of ethylaniline suggested at once the use of a very large excess of bromide of ethyl, by which the formation of one compound only was secured. The mixture assumed a light-yellow colour, turned gradually brown, and deposited after five days four-sided tables of considerable size and remarkable beauty. The mother-liquor was coloured bromide of ethyl, leaving, when distilled off, a small quantity of the same crystalline compound.

The substance in question was, as a subsequent analysis will prove, the pure hydrobromate of a new base, which is represented by the formula—



*i. e.* of ethylaniline in which 1 equiv. of hydrogen is replaced by ethyl, or aniline in which 2 equivs. of the same radical are substituted for a corresponding number of hydrogen-equivalents, or lastly ammonia, in which the three equivalents of hydrogen are replaced, the one by phenyl, the two others each by ethyl.

The formation of this new substance, for which I propose the name diethylaniline or diethylophenylamine, requires no farther illustration: it is absolutely analogous to the production of ethylaniline.

#### *Diethylaniline (Diethylophenylamine).*

The preparation of this compound in a state of purity resembles that of the preceding base, whose physical properties have been only slightly modified by the introduction of the second equivalent of ethyl. The specific gravity was found to be 0.939 at 18°, showing a slight decrease when compared with that of ethylaniline (0.954). The boiling-point, however, was raised nearly 10 degrees; diethylaniline boils quite constantly at 213°.5. Diethylaniline is moreover distinguished from ethylaniline by re-

maining perfectly bright and colourless when exposed to the air. Like ethylaniline it still imparts a yellow colour to fir-wood, but, like the former, fails to affect a solution of hypochlorite of lime.

Analysis performed with protoxide of copper gave the following results:—

0·2301 grm. of oil gave 0·6814 grm. of carbonic acid and 0·2118 grm. of water.

The formula



requires the following values, which may be placed in juxtaposition with the percentage deduced from the above analysis.

	Theory.		Experiment.
20 equivs. of Carbon . . . .	120	80·53	80·76
15 equivs. of Hydrogen . . . .	15	10·06	10·22
1 equiv. of Nitrogen . . . .	14	9·41	—
1 equiv. of Diethylaniline . .	149	100·00	

To obtain farther evidence for the formula of this compound, both the hydrobromate and the platinum-salt were subjected to analysis.

#### *Hydrobromate of Diethylaniline.*

I have mentioned this salt when speaking of the formation of the second base. It is extremely soluble, and resembles in every respect the corresponding ethylaniline-compound. The bromine-determination gave the following results:—

0·4277 grm. of salt gave 0·3490 grm. of bromide of silver.

I place the experimental percentage of hydrobromic acid in juxtaposition with the theoretical value of the formula

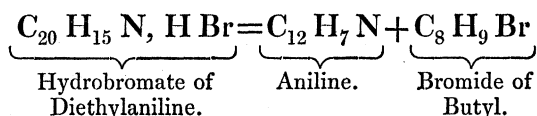


	Theory.		Experiment.
1 equiv. of Diethylaniline . . . . .	149	64·78	—
1 equiv. of Hydrobromic acid . . . . .	81	35·22	35·14
1 equiv. of Hydrobromate of Diethylaniline	230	100·00	

The hydrobromate of diethylaniline, when gently heated, fuses and sublimes like the corresponding aniline- and ethylaniline-salts. When rapidly heated, it is entirely converted into a colourless oil, which distils over. This oil contains equal equivalents of bromide of ethyl and ethylaniline. By this distillation we obtain indeed the very constituents from which the hydrobromate was originally prepared, and which would of course reconvert themselves into hydrobromate of diethylaniline. Only a trifling amount of undecomposed hydrobromate covers, after the distillation is finished, the sides of the retort in the form of a radiated coating.

The peculiar deportment then of the hydrobromates of the ethyl-bases, and probably of all their salts, allows us to remove the several equivalents of ethyl one after

the other from our fabric in the same manner as we had inserted them. When first I became acquainted with diethylated aniline, having then already observed the deportment of the salts of ethylaniline, which under the influence of heat are reconverted into aniline, I indulged for a moment in the pardonable illusion, that the salt of diethylaniline would exhibit the metamorphosis—



a mode of reaction which would have afforded a passage from the ethyl- into the butyl-series. This step however is reserved for a more fortunate experimenter.

*Platinum-salt of Diethylaniline.*

This salt resembles the corresponding compound of ethylaniline. On addition of a concentrated solution of bichloride of platinum to the hydrochlorate, it is precipitated in form of a deep orange-coloured oil, which rapidly solidifies into a hard crystalline mass. If the solutions are mixed in a dilute state, the salt is separated after some time in cross-like yellow crystals. It is not nearly so soluble in water and alcohol as the ethylaniline-salt. Analysis led to the following numbers :—

\*I. 0·1715 grm. of platinum-salt gave 0·2125 grm. of carbonic acid and 0·0700 grm. of water.

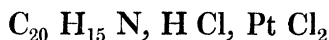
\*II. 0·1848 grm. of platinum-salt gave 0·0513 grm. of platinum.

III. 0·5361 grm. of platinum salt gave 0·1476 grm. of platinum.

IV. 0·5550 grm. of platinum-salt gave 0·1533 grm. of platinum.

	Percentage-composition.			
	I.	II.	III.	IV.
Carbon . . . . .	33·78	—	—	—
Hydrogen . . . . .	4·53	—	—	—
Platinum . . . . .	—	27·76	27·53	27·62

The formula



requires the following values, which I place in juxtaposition with the mean of the experimental results :—

	Theory.		Mean of experiments.
20 equivs. of Carbon . . .	120·00	33·78	33·78
16 equivs. of Hydrogen . .	16·00	4·54	4·53
1 equiv. of Nitrogen . . .	14·00	3·91	—
3 equivs. of Chlorine . . .	106·50	29·99	—
1 equiv. of Platinum . . .	98·68	27·78	27·66
1 equiv. of Platinum-salt . .	355·18	100·00	

\* I. and II. are of a specimen recrystallized from alcohol.

I have not examined any other of the salts of diethylaniline: their deportment resembles in every respect that of the ethylaniline-salts.

#### ACTION OF BROMIDE OF ETHYL ON DIETHYLANILINE.

If we assume that the series of bases, aniline, ethylaniline and diethylaniline, arise from the gradual elimination of the three equivalents of hydrogen in ammonia, and their substitution by 1 equivalent of phenyl and 2 equivalents of ethyl, it is difficult to imagine that bromide of ethyl should have any farther action on diethylaniline, this compound ammonia containing, according to this view, no longer any replaceable hydrogen. However, it would have been deserting the path of inductive research, if this point had been left unestablished by rigorous experiments.

For this purpose diethylaniline was left in contact with bromide of ethyl for nearly a month. After the lapse of this time the mixture had undergone no change in its appearance. On treating however a portion with water, it was found that a small quantity of hydrobromate dissolved, from which on addition of potassa an oily base was separated. The quantity obtained in this manner from nearly two ounces of the united liquids being insufficient for a determination, I subjected a similar mixture, in a sealed tube, for several days to the temperature of boiling water. I was surprised to find that a yellow layer began to separate at the lower extremity of the tube, which increased gradually to a fifth of the liquid column. When allowed to cool, this layer solidified into a crystalline mass. On opening the tube, it was found that there was no pressure from within, except that exerted by the elasticity of bromide of ethyl. After separation of the excess of the bromide by distillation in the water-bath, water added to the viscid residue dissolved the crystals, while an oil floated upon the surface which was found to be entirely basic: it was separated by a distillation at a higher temperature, when it was carried over with the vapour of the water. The remaining liquid in the retort was found to be a solution of a hydrobromate. It was decomposed with potassa, and the liberated base separated from the bromide of potassium by distillation. The two basic oils obtained in this manner, when dissolved in hydrochloric acid and precipitated by bichloride of platinum, gave rise to the formation of two splendid platinum-salts. These salts left on ignition the following percentage of platinum; I. being the oil which had not been in combination; II. the base which had been separated from the hydrobromate.

I. 0.5626 grm. of platinum-salt left 0.1559 grm. of platinum.

II. 0.5384 grm. of platinum-salt left 0.1495 grm. of platinum.

Experimental percentage of platinum,

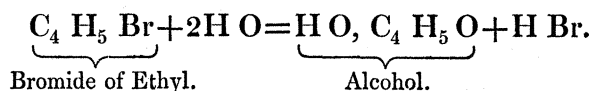
Experimental percentage of platinum,	
I.	II.
27.70	27.76

Theoretical percentage in diethylaniline-platinum-salt.

27.78.

These experiments prove that the basic oil obtained on direct distillation, or by distilling after treatment with potassa, had not assimilated a farther equivalent of

the alcohol-radical ; but the question arose in what manner a portion of the base had been converted into hydrobromate? It was not impossible that the bromide of ethyl, although it had been in contact with chloride of calcium, might nevertheless still have retained a portion of water, whose elements could have induced a regeneration of alcohol with simultaneous formation of hydrobromic acid :



I now took care that both substances, the diethylaniline and the bromide of ethyl, should be perfectly dry before coming into contact. For this purpose, both liquids were left for several days over anhydrous caustic baryta and then subjected to distillation. The compounds at the common temperature were found to have no action upon one another. In order to place them in a condition most favourable for mutual action, the mixture was exposed for several days in a sealed tube to the temperature of boiling water. On opening the tube and extracting the mixture with water, a small quantity of hydrobromate was found to have nevertheless been formed. The portion insoluble in water was dissolved in hydrochloric acid and precipitated by bichloride of platinum. The salt obtained in this manner could not be mistaken. It fell down in the form of a yellow oil, which rapidly solidified into the orange-yellow crystalline aggregates characterizing the diethylaniline-compound.

From these experiments, it would appear that diethylaniline is no longer capable of fixing another equivalent of ethyl. Still the production of the small quantity of hydrobromate in the *last* experiment indicates that the phenomenon cannot be due to the formation of alcohol. Farther steps are necessary for the explanation of this transformation.

---

In aniline, ethylaniline and diethylaniline, then we have three bases, which may be considered as derived from ammonia by the elimination and replacement of its three hydrogen-equivalents. The successive formations of ethylaniline and diethylaniline from aniline have been detailed in the preceding paragraphs ; the passage of ammonia into aniline, when exposed to the action of a phenyl-compound, has been proved at an earlier period by some experiments, made jointly by M. LAURENT and myself, upon the action, at a high temperature, of hydrated oxide of phenyl on ammonia. In this reaction a small but unequivocal quantity of aniline is formed.

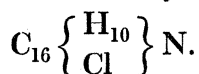
The formation of aniline, ethylaniline and diethylaniline, appeared to have established in a sufficiently satisfactory manner, the point of theory which is here in question ; still I thought desirable the acquisition of additional facts in support of the position to which this inquiry has conducted me. Thus I have been led to study the action of bromide of ethyl upon several of the derivatives of aniline, and to try whether other alcohol-radicals, such as methyl and amyl, would have a similar

action; lastly, in order to complete the investigation, I was obliged to leave the amidogen-bases altogether in order to submit the typical ammonia itself to examination.

Among the bases derived from aniline, there is a class whose deportment with bromide of ethyl appeared to be more particularly worthy of a careful investigation. This is the group of compounds produced from aniline by substitution, and embracing chloraniline, dichloraniline and trichloraniline, the corresponding bromanilines, iodaniline and nitraniline. The question arose in what manner will these substances, in which the original aniline has lost already a certain quantity of its hydrogen, comport themselves under the influence of bromide of ethyl? The answer afforded by experiment was unequivocal and in perfect accordance with the result anticipated by theory, although it may here at once be stated, that the difficulty of obtaining the compounds in question in sufficient quantity has prevented me from pursuing this part of the investigation as far as I could have wished.

#### ACTION OF BROMIDE OF ETHYL UPON CHLORANILINE.

A solution of chloraniline in dry bromide of ethyl exhibits no apparent change even after several days' exposure to the temperature of boiling water. On adding however water and distilling off the excess of bromide of ethyl, it was found that the chloraniline had been converted into a hydrobromate, which was held in solution, scarcely a trace of uncombined base being left. Addition of potassa to the solution of the hydrobromate separated at once a yellow oily base, of a very characteristic aniseed-odour, differing from chloraniline in many respects. It remained liquid even at the temperature of a cold winter day, while chloraniline is distinguished by the facility with which it crystallizes. Its salts are much more soluble than the corresponding chloraniline-salts: I have only seen the sulphate and oxalate in a crystallized state. This liquid base is evidently ethylochloraniline—



I am sorry that I have not been able to verify this formula by direct analysis. The amount of substance at my disposal precluded the idea of submitting it to the processes of purification necessary before combustion. I had hoped to fix its composition by the determination of the platinum in the platinum-salt. Unfortunately this salt separated in the form of a yellow oil, which could not by any means be made to crystallize. Obligated to desist from direct analysis, I endeavoured to gain the requisite data by another mode of proceeding.

#### ACTION OF BROMIDE OF ETHYL UPON ETHYLOCHLORANILINE.

Recollecting that in almost all the instances which I have examined, the tendency exhibited by the various bases of producing readily crystallizable platinum-salts increased with the degree of their ethylation, I subjected the whole amount of the



still hypothetical ethylochloraniline, after having dried it by a current of hot air, to the action of a considerable excess of bromide of ethyl. After two days' exposure to  $100^{\circ}$  the mixture was found to contain a hydrobromate in solution, not a trace of free base being left. There was no doubt that a second equivalent of ethyl had been assimilated. On decomposing the hydrobromate with potassa, an oil separated resembling, in its appearance and also in its odour, the preceding compound. An attempt to purify the ethylochloraniline from the potassa by distillation with water having failed, on account of the high boiling-point of this substance, the purification of the diethylochloraniline, for as such the new compound was to be considered, was at once effected with ether. The ethereal solution of the oil was carefully washed with water to remove adhering potassa, and evaporated: the yellow oil remaining after this treatment was dissolved in hydrochloric acid, and the solution mixed with bichloride of platinum. Immediately a splendid orange-yellow crystalline precipitate was separated, which after washing with water was fit for analysis. This salt fused at  $100^{\circ}$ .

In the analysis a small quantity of platinum was lost.

0.2376 grm. of platinum-salt gave 0.0583 grm. of platinum.

The formula



requires the following values:—

	Theory.		Experiment.
1 equiv. of Diethylochloraniline .	183.50	47.09	—
1 equiv. of Hydrochloric acid . .	36.50	9.37	—
2 equivs. of Chlorine . . . . .	71.00	18.22	—
1 equiv. of Platinum . . . . .	98.68	25.32	24.53
1 equiv. of Platinum-salt . . .	389.68	100.00	

The result, although somewhat below theory, shows that chloraniline, when subjected to the action of bromide of ethyl, exhibits absolutely the same deportment as aniline itself, two equivalents of ethyl being consecutively introduced which give rise to the formation of two new terms, which demand the names ethylochloraniline (ethylochlorophenylamine) and diethylochloraniline (diethylochlorophenylamine).

#### ACTION OF BROMIDE OF ETHYL UPON BROMANILINE.

The absolute analogy existing between chloraniline and bromaniline, to which I have alluded in a former paper\*, is maintained also in the deportment of these two substances towards bromide of ethyl. Bromaniline is rapidly converted into hydrobromate of ethylobromaniline which could not, except by analysis, be distinguished from the corresponding chlorine-base. The platinum-salt being likewise a viscid oil,

\* Chem. Soc. Mem. ii. 291.

I have omitted to analyse it. There is however no doubt about the existence of an ethylobromaniline,



I have not attempted to ethylate this compound any farther.

#### ACTION OF BROMIDE OF ETHYL UPON NITRANILINE.

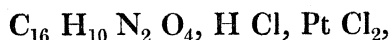
##### *Ethylonitriline (Ethylonitrophenylamine).*

Nitriline readily dissolves in bromide of ethyl. The solution soon deposits, even at the common temperature, pale-yellow crystals of considerable size. At the boiling temperature of water the conversion is rapidly accomplished. On addition of an alkali to the hydrobromate, the ethylonitriline separates as a brown oily mass, which solidifies after some time with crystalline structure. In this substance, as well as in the other ethylated bases, the properties of the mother-compound are only slightly modified. Thus we find in the base ethylonitriline still the yellow colour of nitriline, which it readily imparts to the skin, but which it loses altogether in its salts. These salts are as easily soluble in water as the corresponding nitriline-compounds, if not even more so, and possess the same peculiar sweetish taste; they all crystallize however on evaporating their solutions nearly to dryness. Ethylonitriline dissolves readily in ether and alcohol, less so in boiling water; from a solution in the latter the base is deposited in stellated groups of yellow crystals, which are readily distinguished from the felted mass of long needles, separated on cooling from an aqueous solution of nitriline.

I have fixed the composition of ethylonitriline by a single number, namely, by the determination of the metal in the platinum double salt. This compound is prepared by adding bichloride of platinum to a very concentrated solution of the hydrochlorate; this must not contain much free acid, in which the salt would redissolve. After a short time pale-yellow scales are separated, which have to be washed with cold water. The small quantity of substance at my disposal may excuse the slight deficiency in the amount of platinum.

0.1544 grm. of ethylonitriline gave 0.0405 grm. of platinum.

This percentage agrees with the formula



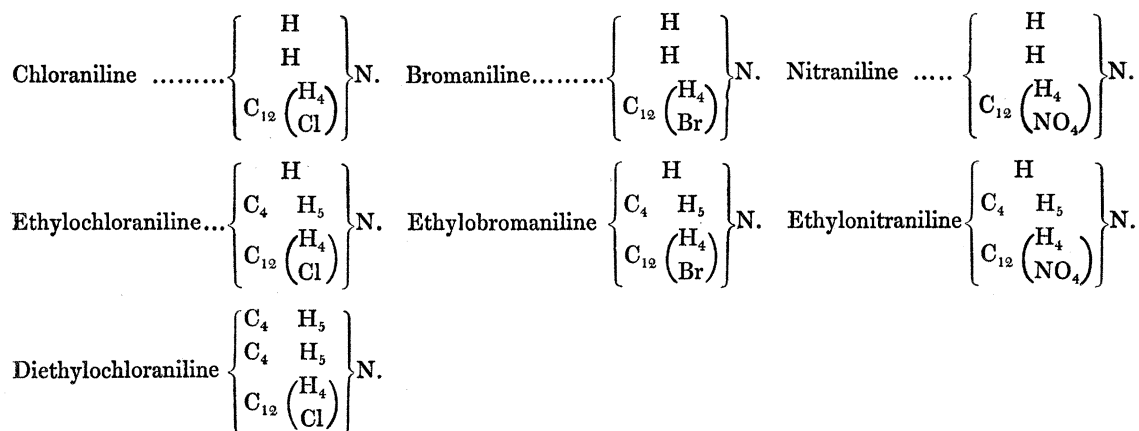
as will be seen from the following comparison:—

	Theory.		Experiment.
1 equiv. of Ethylonitriline .	166.00	44.60	—
1 equiv. of Hydrochloric acid	36.50	9.80	—
2 equivs. of Chlorine . . .	71.00	19.09	—
1 equiv. of Platinum . . .	98.68	26.51	26.23
1 equiv. of Platinum-salt . .	372.18	100.00	

The nitraniline-salt contains 28·66 per cent of platinum. I have not prepared a diethylnitraniline.

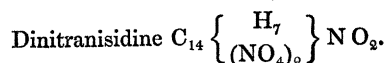
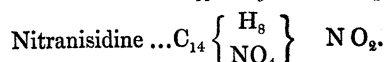
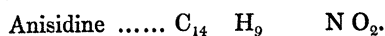
The deportment of chloraniline, bromaniline and nitraniline with bromide of ethyl, appears to throw much light upon the constitution of these substitution-bases. The possibility of introducing into these substances two equivalents of ethyl, shows that they must contain the same amount of basic hydrogen (an expression by which I may be allowed to represent briefly the hydrogen of the ammonia-skeleton) as aniline itself, and hence it is evident that it was the hydrogen of the phenyl which was replaced by chlorine, bromine and hyponitric acid in the transformation of aniline into its chlorinated, brominated, &c. relatives.

This transformation is due to a secondary substitution affecting the hydrogen in the radical, which replaced the original ammonia-hydrogen; and the constitution of the substances in question may hence be graphically represented by the following formulæ:—



This mode of viewing their constitution is in perfect harmony with the facts at present in our possession, both as regards the deportment of the substitution-anilines, and the substances similarly derived from hydrated oxide of phenyl. Experiment has shown that in aniline 1, 2 or 3 equivalents of hydrogen may be replaced by chlorine, bromine, and probably also by the elements of hyponitric acid\*. In these substances their basic properties gradually diminish with the successive insertions

\* At the present moment we have only nitraniline, but it is scarcely to be doubted that we shall soon become acquainted with the nitro-term corresponding to dichloraniline and trichloraniline. Recent researches of M. CAHOURS (Ann. Ch. Phys. sér. xxvii. 439) on the derivatives of anisole have pointed out the first alkalioid containing 2 equivs. of hyponitric acid.



In this series only the trinitranisidine  $\text{C}_{14} \left\{ \begin{array}{c} \text{H}_6 \\ (\text{NO}_4)_3 \end{array} \right\} \text{N O}_2$  is wanting.

of chlorine or bromine into the compound. Bromaniline still retains a strongly alkaloidal character which in dibromaniline is so far impaired that by simple ebullition it is separated from its aqueous saline solutions; tribromaniline, lastly, is a perfectly indifferent compound. Now if we recollect that in monobrominated and dibrominated phenole (obtained by M. CAHOURS, by distilling respectively, bromosalicylic and dibromosalicylic acid), the original character of hydrated oxide of phenyl is gradually altered and becomes in tribromophenole (bromophenisic acid of M. LAURENT) powerfully acid, we cannot be surprised to find that the gradual development of electronegative properties in the radical should affect the nature of a basic system in which it replaces hydrogen. We have two parallel groups of bodies, the chemical character of which is differently affected by the modification induced in the radical, existing in both, by the assimilation of bromine.

Hydrated protoxide of phenyl .....	$\left. \begin{array}{l} \text{HO, C}_{12} \text{ H}_5 \text{ O, slightly acid.} \end{array} \right\}$	Phenylamine .....	$\left. \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12} \text{ H}_5 \end{array} \right\}$	N, powerfully basic.
Bromophenole .....	$\text{HO, C}_{12} \left\{ \begin{array}{c} \text{H}_4 \\ \text{Br} \end{array} \right\} \text{O, more so.}$	Bromophenylamine ...	$\left. \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12} \left( \begin{array}{c} \text{H}_4 \\ \text{Br} \end{array} \right) \end{array} \right\}$	N, less so.
Dibromophenole ...	$\text{HO, C}_{12} \left\{ \begin{array}{c} \text{H}_3 \\ \text{Br}_2 \end{array} \right\} \text{O, more so.}$	Dibromophenylamine	$\left. \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12} \left( \begin{array}{c} \text{H}_3 \\ \text{Br}_2 \end{array} \right) \end{array} \right\}$	N, less so.
Tribromophenole Bromophenisic acid	$\left. \begin{array}{l} \text{HO, C}_{12} \left\{ \begin{array}{c} \text{H}_2 \\ \text{Br}_3 \end{array} \right\} \text{O, powerfully acid.} \end{array} \right\}$	Tribromophenylamine	$\left. \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12} \left( \begin{array}{c} \text{H}_2 \\ \text{Br}_3 \end{array} \right) \end{array} \right\}$	N, neutral.

Tribromophenylamine (tribromaniline) is a compound differing in its nature in no way from oxamide. Both these substances are ammonia, whose basic character has been counterbalanced by the insertion of a powerfully electronegative radical in the place of one of the hydrogen-equivalents. These two substances, when subjected to the influence of strong acids, comport themselves in exactly the same manner; they both reproduce ammonia, the one with formation of tribromophenisic, the other of oxalic acid.

The paragraphs now following are devoted to a brief account of the bases derived from aniline by the insertion of methyl and amyl. I have not however followed out the examination of these substances to the same extent, the principle having been in fact sufficiently established by the formation of the ethyl bodies.

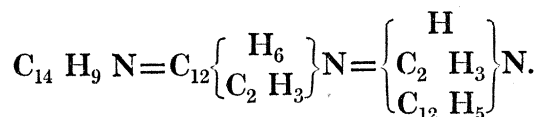
## ACTION OF BROMIDE AND IODIDE OF METHYL UPON ANILINE.

*Methylaniline (Methylophenylamine).*

The deportment of aniline with bromide of methyl resembles its behaviour with the ethyl-compound. The mixture rapidly solidifies into a crystalline mass of hydrobromate of methylaniline. Bromide of methyl being extremely volatile, I have used also the iodide, which boils at a more convenient temperature. The action of the latter compound upon aniline is very remarkable, the evolution of heat, on mixing the two substances, being so great, that the liquid enters into violent ebullition, so that unless the substances be mixed gradually, the crystalline hydriodate, which is formed immediately, is actually thrown out of the vessel.

Methylaniline, when separated from the hydrobromate or hydriodate, appears as a transparent oil of a peculiar odour, somewhat different from that of aniline, and boiling at  $192^{\circ}$ ; it has retained the properties of aniline in a higher degree than the ethylated compound. This substance yields still the blue coloration with hypochlorite of lime, although in a less degree than aniline. Its salts are less soluble than those of ethylaniline; they are at once formed in the crystalline state on addition of the respective acids; the oxalate crystallizes very easily, but is rapidly decomposed with reproduction of aniline, and probably with formation of oxalate of methyl\*.

The composition of methylaniline is represented by the expression



I have established this formula by the analysis of the platinum-salt. This is precipitated as a transparent oil, which rapidly changes into pale-yellow crystalline tufts, resembling the corresponding aniline-salt, but liable to rapid decomposition. The washing must be quickly done, for the salt is extremely soluble in water, and must be immediately followed by desiccation. Even when very carefully prepared, it has become dark by the time it is ready for combustion. It turns instantaneously black if an alcoholic solution of the hydrochlorate be employed for its preparation.

Analysis I. refers to a salt obtained with the base prepared by means of the bromide; for analysis II. the base had been formed by the iodide. The specimen analysed under III. again had been obtained with the bromide, but it was in an advanced state of decomposition, and had in consequence become perfectly black.

I. 0.1018 grm. of platinum-salt gave 0.0319 grm. of platinum.

II. 0.2467 grm. of platinum-salt gave 0.0784 grm. of platinum.

III. 0.2065 grm. of platinum-salt gave 0.0660 grm. of platinum.

\* The aniline thus reproduced was identified by the analysis of the platinum-compound.

0.7910 grm. of platinum-salt gave 0.2615 grm. of platinum.

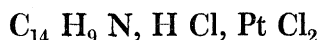
Experimental.      Theoretical percentage of platinum in aniline-platinum-salt.

33.05

32.98

Percentage of platinum.		
I.	II.	III.
31.33	31.78	31.96.

The formula



requires the following values:—

	Theory.		Mean of I. and II.
1 equiv. of Methylaniline . .	107.00	34.16	—
1 equiv. of Hydrochloric acid .	36.50	11.65	—
2 equivs. of Chlorine . . .	71.00	22.67	—
1 equiv. of Platinum . . . .	98.68	31.52	31.55
1 equiv. of Platinum-salt . .	313.18	100.00	

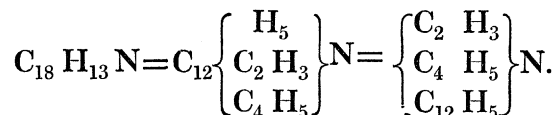
I have not attempted to form a dimethylaniline.

#### ACTION OF IODIDE OF METHYL UPON ETHYLANILINE.

##### *Methylethylaniline (Methylethylophenylamine).*

I have established the existence of this compound merely by qualitative experiments. The mixture of ethylaniline and iodide of methyl begins to crystallize after two days' exposure to the temperature of boiling water. Methylethylaniline resembles the preceding base in its odour, but has no longer any action upon hypochlorite of lime. I had not prepared a sufficient quantity of the compound for a determination of the boiling-point. The salts of this base are extremely soluble. With the exception of the hydrobromate, I have not been able to obtain a single one in crystals. Even the platinum-salt is not to be obtained in the crystalline form; it is extremely soluble, and separates, if very concentrated solutions be employed, as a yellow oil, which does not solidify even after lengthened exposure to the air. This circumstance has prevented me from fixing the composition of methylethylaniline by a number.

It cannot however be doubted that it is represented by the formula—



This compound presents a certain degree of interest, inasmuch as the 3 equivs. of hydrogen in the ammonia are replaced by three different radicals, namely by methyl, ethyl and phenyl. I have prepared however a similar compound containing, instead of methyl, amyl, whose properties permitted an easier analysis.

## ACTION OF BROMIDE OF AMYL UPON ANILINE.

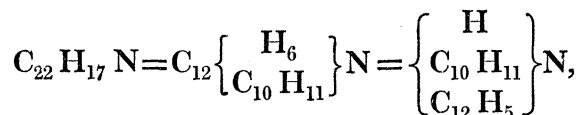
*Amylaniline (Amylophenylamine).*

A mixture of aniline and an excess of bromide of amyl, when left in contact at the common temperature for some days, deposits magnificent crystals of hydrobromate of aniline. Never have I obtained this salt in larger and more definite crystals; although I have seen it deposited of late from a good many solutions. The mother-liquor of this salt is a mixture of amylaniline and bromide of amyl. If aniline be heated in the water-bath with a very large excess of bromide of amyl, the whole is converted into hydrobromate of amylaniline, which remains dissolved in the excess of bromide.

When prepared without the co-operation of heat, the amylaniline may be purified simply by separating the crystals of the aniline-salt and distilling the remaining mixture, when the bromide of amyl passes over long before the amyl-base begins to volatilize. If the base has been produced by heating the mixture, it is necessary, after the excess of bromide has been removed, to distil the hydrobromate with potassa. On submitting the base, purified in the usual manner, to combustion, the following numbers were obtained:—

0·2760 grm. of oil gave 0·8161 grm. of carbonic acid, and 0·2560 grm. of water.

This analysis leads to the formula—



as may be seen from a juxtaposition of the theoretical and experimental values.

	Theory.		Experiment.
22 equivs. of Carbon . . . . .	132	80·98	80·64
17 equivs. of Hydrogen . . . . .	17	10·42	10·30
1 equiv. of Nitrogen . . . . .	14	8·60	—
1 equiv. of Amylaniline . . . . .	163	100·00	

Amylaniline is a colourless liquid, possessing all the family-features of the group. It is distinguished, at the common temperature, by a very agreeable, somewhat rose-like odour, rather an unusual property for an amyl-compound; however, it does not deny its origin, for on heating the base the disgusting odour of the fusel-alcohol appears but slightly modified. Amylaniline boils constantly at 258°, or 54=3×18° higher than ethylaniline. This boiling-point is characteristic, inasmuch as the elementary group amyl raises the boiling-point of aniline 44° higher than does the insertion of two equivalents of ethyl, whose weight is not very inferior to that of the single amyl-equivalent.

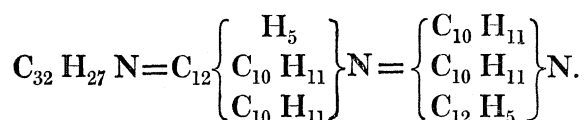
The amyl-base forms beautiful rather insoluble salts with hydrochloric, hydro-

bromic and oxalic acids; when heated with water, they form an oily layer on the surface, and crystallize only slowly on cooling: they have the peculiar fatty appearance which characterizes the crystalline amyl-compounds. The platinum-salt is precipitated as a yellow mass of an unctuous consistence; it crystallizes but very slowly, and usually not before partial decomposition has set in. It is on this account that I have not made an analysis of this compound.

#### ACTION OF BROMIDE OF AMYL UPON AMYLANILINE.

##### *Diamylaniline (Diamylophenylamine).*

A mixture of amylaniline and bromide of amyl solidifies after two days' exposure to the temperature of the water-bath. The new basic compound, when separated and purified in the usual manner, resembles the preceding base, especially with respect to odour. Its salts are so insoluble in water that at the first glance one is almost inclined to doubt the basicity of the substance, inasmuch as the oil appears to be perfectly insoluble in dilute hydrochloric and sulphuric acids. However, the oily drops floating in the acid solution are the salts themselves, which gradually solidify into splendid crystalline masses, having likewise the fatty appearance of amyl-substances. The composition of diamylaniline is represented by the expression—



I have established this formula by the analysis of the platinum-compound, which is precipitated as an oily mass, rapidly solidifying into a brick-red crystalline substance. If an alcoholic solution of the hydrochlorate be employed, it is immediately obtained in the crystalline state. When exposed to the heat of the water-bath this salt fuses, without however undergoing any decomposition.

On analysis the following results were obtained:—

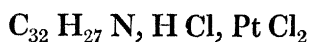
I. 0.3015 grm. of platinum-salt gave 0.4820 grm. of carbonic acid, and 0.1765 grm. of water.

II. 0.2550 grm. of platinum-salt gave 0.0572 grm. of platinum.

III. 0.4750 grm. of platinum-salt gave 0.1061 grm. of platinum.

	Percentage.		
	I.	II.	III.
Carbon . . . . .	43.60	—	—
Hydrogen . . . . .	6.50	—	—
Platinum . . . . .	—	22.43	22.34

The formula





requires the following values :—

	Theory.		Experiment.
32 equivs. of Carbon . . . .	192·00	43·71	43·60
28 equivs. of Hydrogen . . . .	28·00	6·37	6·50
1 equiv. of Nitrogen . . . .	14·00	3·19	—
3 equivs. of Chlorine . . . .	106·50	24·25	—
1 equiv. of Platinum . . . .	98·68	22·47	22·38
1 equiv. of Platinum-salt . . .	439·18	100·00	

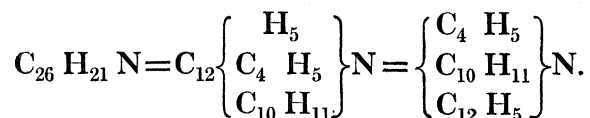
Diamylaniline boils between 275° and 280°: the small scale upon which I had to work prevented me from determining it more accurately. It is interesting to see how very little the boiling-point is raised by the introduction of the second equivalent of amyl, when compared with the effect produced by the insertion of the first. The same remark applies to the ethylanilines.

#### ACTION OF BROMIDE OF ETHYL UPON AMYLANILINE AND OF BROMIDE OF AMYL UPON ETHYLANILINE.

##### *Amylethylaniline (Amylethylophenylamine).*

It remained now only to analyse a basic compound in which the three equivalents of the ammonia-hydrogen should be replaced by three different radicals. I found in amylethylaniline a substance similar in composition to methylethylaniline, but which by its properties admitted of a rigorous analytical examination.

Amylethylaniline is formed without difficulty by the action of bromide of ethyl upon amylaniline. The mixture having been exposed to the heat of the water-bath, the conversion was found to be complete after two days. When purified in the usual way, amylethylaniline forms a colourless oil, boiling at 262°, only 4° higher than the amyl-base. The properties of this substance are analogous to those of the other bases. It forms a beautiful crystalline hydrochlorate and hydrobromate; the platinum-salt is precipitated in form of a light orange-yellow pasty mass, which rapidly crystallizes. This salt fuses at 100°. By analysis of the platinum-compound I was enabled to fix without difficulty the composition of the base, which is represented by the formula



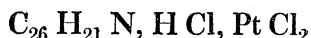
I. 0·2893 grm. of platinum-salt gave 0·4137 grm. of carbonic acid, and 0·1495 grm. of water.

II. 0·2647 grm. of platinum-salt gave 0·0652 grm. of platinum.

III. 0·2510 grm. of platinum-salt gave 0·0619 grm. of platinum.

	Percentage-composition.		
	I.	II.	III.
Carbon . . . . .	39.00	—	—
Hydrogen . . . . .	5.70	—	—
Platinum . . . . .	—	24.63	24.66

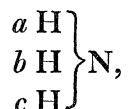
The formula



requires the following values :—

	Theory.		Experiment.
26 equivs. of Carbon . . . . .	156.00	39.27	39.00
22 equivs. of Hydrogen . . . . .	22.00	5.54	5.70
1 equiv. of Nitrogen . . . . .	14.00	3.53	—
3 equivs. of Chlorine . . . . .	106.50	26.81	—
1 equiv. of Platinum . . . . .	98.68	24.84	24.64
1 equiv. of Platinum-salt . . . . .	397.18	100.00	

A substance of exactly the same composition as amylethylaniline may be obtained by the action of bromide of amyl upon ethylaniline. I was led to prepare this compound by some ideas which had suggested themselves in a perfectly different line of experiments. I wished to ascertain whether the several hydrogen-equivalents in ammonia were of the same value, if I may use this expression, or in other words, whether it was indifferent which of the three equivalents was replaced by a given radical. Supposing that in ammonia



it is the  $a$  hydrogen which is replaced by phenyl, the question arose whether the same substance would be formed, for instance, by substituting amyl and ethyl, either for  $b$  and  $c$ , or for  $c$  and  $b$ .

I have carefully compared the properties of amylethylaniline, by which name I designate the compound produced by the action of bromide of ethyl upon amylaniline with those of ethylamylaniline obtained by acting with bromide of amyl upon ethylaniline, and find that these substances comport themselves in every respect perfectly alike.

A last and decisive argument was hoped to be gained from the deportment of the salts of these bases, when subjected to the influence of heat. For this purpose the hydrobromates were prepared. When distilled, both these salts were split into bromide of amyl and ethylaniline; I hence assume that the action of bromide of ethyl upon amylaniline, and that of bromide of amyl upon ethylaniline, give rise to the formation of exactly the same basic compound.

## ACTION OF BROMIDE OF ETHYL UPON AMMONIA.

After the termination of the experiments which have been detailed in the preceding pages, there remained no doubt in my mind respecting the deportment which ammonia itself would exhibit when subjected in a similar manner to the influence of bromide of ethyl. I had a right to expect in this reaction the consecutive formation of three alkaloids, differing from ammonia by containing respectively one, two or the three equivalents of hydrogen replaced by ethyl.

Experiment has realized this expectation in a very satisfactory manner. I intend to give here only an outline of the process employed, and a short description of the substances obtained, together with some characteristic numbers, fixing beyond a doubt the composition of the new bases formed under these circumstances. I hope that I shall soon be able to communicate a more detailed account of these compounds, as well as of the bases belonging to the methyl- and amyl-series.

*Formation of Ethylamine (Ethylammonia).*

Bromide of ethyl acts very slowly on an aqueous solution of ammonia in the cold. Action however takes place; after the lapse of a week or ten days the solution contains a considerable quantity of a hydrobromate in solution. This hydrobromate is a mixture of the salts of ammonia and ethylamine, the base discovered by M. WURTZ on decomposing cyanate of ethyl with potassa. The presence of this compound may be readily proved by evaporating the liquid, after the separation of the excess of bromide of ethyl, to dryness in the water-bath, in order to drive off alcohol which might have possibly been formed. On adding potassa-solution to the solid residue, an alkaline gas is at once evolved, which burns with the pale-blue flame of ethylamine.

If an alcoholic solution of ammonia be substituted for the aqueous liquid, the decomposition proceeds more rapidly. After twenty-four hours a copious crystalline precipitate of bromide of ammonium has been deposited. The mother-liquor contains hydrobromate of ethylamine and the base in the free state.

The action of bromide of ethyl upon ammonia may be considerably accelerated by raising the temperature to the boiling-point of water. I found it convenient to introduce a concentrated solution of ammonia, with an excess of bromide of ethyl, into pieces of combustion-tube 2 feet in length. These tubes, after having been carefully sealed before the blowpipe, were immersed to the height of about half a foot into boiling water. The bromide of ethyl enters at once into lively ebullition, rises through the supernatant layer of ammonia, condenses in the upper part of the tube, which is cold, and falls down to commence again the same circulation. During this process the bromide of ethyl diminishes rapidly in volume. The reaction may be considered terminated as soon as a quarter of an hour's ebullition ceases to effect a considerable change in the bulk of the bromide. On opening the tube, the solution

is found to be either neutral or even of an acid reaction, and to contain hydrobromate of ethylamine, which may be separated, by distillation with potassa, with all the properties enumerated by M. WURTZ. I have not to add a single word to the accurate description of this distinguished chemist, and will here only give the analysis of a platinum-salt prepared with ethylamine which had been obtained by this process :—

0·2521 grm. of platinum-salt gave 0·0992 grm. of platinum.

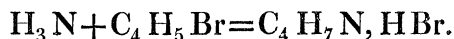
The formula



requires the following values :—

	Theory.		Experiment.
1 equiv. of Ethylamine . . .	45·00	17·91	—
1 equiv. of Hydrochloric acid .	36·50	14·55	—
2 equivs. of Chlorine . . . .	70·00	28·24	—
1 equiv. of Platinum . . . .	98·68	39·30	39·34
1 equiv. of Platinum-salt . . .	260·18	100·00	

The production of ethylamine in this reaction is absolutely analogous to that of ethylaniline ; it is represented by the equation



#### *Formation of Diethylamine (Diethylammonia).*

On treating an aqueous solution of ethylamine in the same manner with an excess of bromide of ethyl, phenomena of a perfectly analogous character are observed. The reaction however proceeds more rapidly and is terminated after a few hours' ebullition. The aqueous layer, which assumes a bright yellow colour, deposits acicular crystals on cooling, consisting of the hydrobromate of a new base, for which I propose the name diethylamine or diethylammonia. This base may be readily separated by distillation with potassa, when it passes over in form of a very volatile and inflammable liquid, which is still extremely soluble in water and of a powerful alkaline reaction. When dissolved in hydrochloric acid and mixed with a concentrated solution of bichloride of platinum, it yields a very soluble platinum-salt, which crystallizes in orange-red grains, very different from the orange-yellow leaves of the corresponding ethylamine-salt.

The analysis of this platinum-salt shows that diethylamine may be viewed as ammonia, in which 2 equivs. of hydrogen are replaced by 2 of ethyl.

0·2250 grm. of platinum-salt gave 0·1430 grm. of carbonic acid, and 0·0890 grm. of water.

0·3413 grm. of platinum-salt gave 0·1210 grm. of platinum.

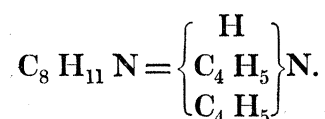
These numbers agree exactly with the formula



which requires the following values :—

	Theory.		Experiment.
8 equivs. of Carbon . . . .	48·00	17·19	17·33
12 equivs. of Hydrogen . . . .	12·00	4·30	4·39
1 equiv. of Nitrogen . . . .	14·00	5·03	—
3 equivs. of Chlorine . . . .	106·50	38·14	—
1 equiv. of Platinum . . . .	98·68	35·34	35·45
1 equiv. of Platinum-salt. . . .	279·18	100·00	

The preceding analyses establish the composition of diethylamine, which is represented by the formula



*Formation of Triethylamine (Triethylammonia).*

This arises from diethylamine in the same manner as the latter from ethylamine : however unlike the deportment observed in the formation of diethylaniline, the rapidity of the action increases with the progress of the ethylation. A mixture of a concentrated solution of diethylamine with bromide of ethyl solidifies after a very short ebullition into a mass of beautiful fibrous crystals, sometimes of several inches in length, being the hydrobromate of a new base, for which I propose the name of triethylamine or triethylammonia. This alkaloid may be readily separated by distillation with potassa, when it presents itself in the form of a light, colourless, powerfully alkaline liquid, still very volatile and inflammable, and also pretty soluble in water, but in a less degree than diethylamine.

To fix the composition of triethylamine, the platinum-salt was subjected to analysis. This is one of the finest salts which I have ever seen. It is extremely soluble in water, and crystallizes on the cooling of concentrated solutions in magnificent orange-red rhombic crystals, which are obtained of perfect regularity and of very considerable size (half an inch in diameter), even if very limited quantities of solution be employed. The analysis of this salt, which slightly fused at 100°, shows that triethylamine may be considered as ammonia, in which the 3 equivs. of hydrogen are replaced by 3 of ethyl.

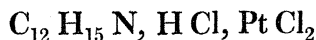
I. 0·5950 grm. of platinum-salt gave 0·5110 grm. of carbonic acid, and 0·2800 grm. of water.

II. 0·1860 grm. of platinum-salt gave 0·0595 grm. of platinum.

III. 0·5230 grm. of platinum-salt gave 0·1679 grm. of platinum.

	Percentage-composition.		
	I.	II.	III.
Carbon . . . . .	23·42	—	—
Hydrogen . . . . .	5·22	—	—
Platinum . . . . .	—	31·99	32·10

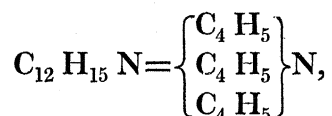
The formula



requires the following values:—

	Theory.		Experiment.
12 equivs. of Carbon . . . . .	72·00	23·43	23·42
16 equivs. of Hydrogen . . . . .	16·00	5·20	5·22
1 equiv. of Nitrogen . . . . .	14·00	4·54	—
3 equivs. of Chlorine . . . . .	106·50	34·71	—
1 equiv. of Platinum . . . . .	98·68	32·12	32·04
1 equiv. of Platinum-salt . . . . .	307·18	100·00	

These numbers are sufficient to establish beyond a doubt the formula



as representing the compound in question.

Although not inclined to expect a farther action of bromide of ethyl upon triethylamine, after the experiments performed with diethylaniline, but hoping to obtain in this series more definite results than the latter had yielded, I thought it important to appeal once more to experiment. A mixture of an aqueous solution of triethylamine and bromide of ethyl, sealed for this purpose into a tube, solidified after two hours' ebullition. The crystals formed in this reaction had the fibrous aspect of the hydrobromate of triethylamine; still among the transparent prisms some white opake granular crystals were observed. To gain more positive information, the excess of bromide of ethyl was volatilized and the residue distilled with potassa. The base obtained in this manner, converted into a platinum-salt and submitted in this form to analysis—

0·1040 grm. of platinum-salt left 0·0334 grm. of platinum.

Experimental percentage.

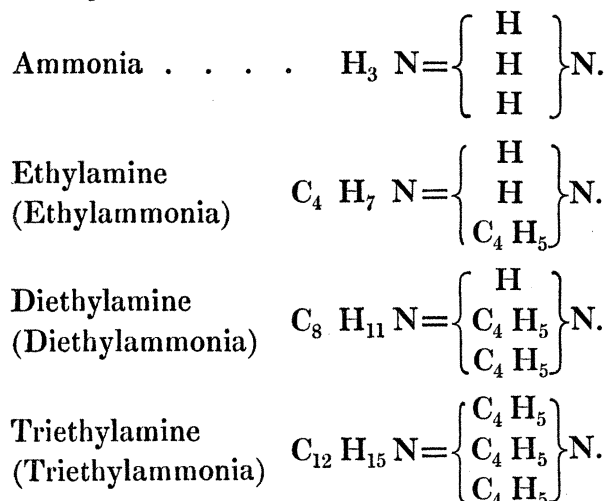
32·11

Theoretical percentage in the platinum-salt  
of triethylamine.

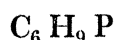
32·11

Accordingly, the base which had distilled over, had evidently not been affected any farther by the influence of bromide of ethyl. The appearance however of the opake crystals indicates that a second compound is formed, whose careful study is necessary for the elucidation of this reaction. I am at present engaged with this part of the inquiry.

The action then of bromide of ethyl upon ammonia gives rise to the formation of the following series of compounds :—



It cannot be doubted for a moment that the same compounds will be obtained in the methyl- and amyl-series, the first terms in each of these series having been actually prepared by M. WURTZ. Nor is it improbable that arseniетted and phosphoretted hydrogen, which, as is well known, imitate to a certain extent the habits of ammonia, when subjected to the action of the chlorides, bromides or iodides of the alcohol-radicals, will yield a series of arseniетted or phosphoretted bases, corresponding to the three classes observed with nitrogen. The highly remarkable bodies discovered by M. PAUL THENARD appear to warrant this expectation as far as the phosphorus-series is concerned, his compound



corresponding evidently in the phosphoretted methyl-series to triethylamine. I mean to extend these researches to the action of the bromides of the alcohol-radicals on phosphoretted and arseniетted hydrogen.

In the preceding pages, I have only endeavoured to establish the composition and the principal physical characters of the new compounds which form the subject of this investigation. To complete their history, it will be necessary to submit to a careful examination their deportment under the influence of the ordinary decomposing agents, and also their behaviour with other organic substances. The study of the imidogen- and nitrile-bases, to use this convenient though only provisional designation, will require particular attention, the character of the amidogen-bases being already pretty well established by the numerous researches respecting aniline, which have been performed within the last few years. We cannot but expect, that, although the general character of all these substances is very nearly the same, their special properties must present considerable diversity, which may be clearly defined by, and even anticipated from, the theoretical conception of their constitution, as deduced from the present investigation. Though fully aware of the dangers threatening the

inquirer as soon as he steps beyond the interpretation of well-established facts, it is difficult to resist the temptation of indulging even now in some speculations on the probable deportment of these alkaloids. In a former paper\* I have pointed out that the methods which convert the ammonia-salts into nitriles, fail to produce a similar effect upon the salts of aniline, while experiment has shown that these salts are capable of producing compounds analogous to the amides, to the amidogen-acids and to the imides. This result is perfectly intelligible if we conceive aniline in the light of an amidogen-base. In the same manner we shall probably see that the imidogen-bases, such as ethylaniline and diethylamine, although still capable of giving rise to the formation of amides and amidogen-acids, will yield no longer compounds representing the imides of the ammonia-salts; in the nitrile-bases, lastly, such as diethylaniline or triethylamine, we shall probably find that the faculty of yielding derivatives by elimination of water is either restricted to the formation of compounds corresponding to the so-called amidogen-acids, or has entirely disappeared.

RELATION OF THE BASES DERIVED FROM ANILINE AND AMMONIA WITH  
OTHER GROUPS OF ALKALOIDS.

It is impossible to leave the history of these compounds without alluding to some remarkable relations existing between these substances and other bodies of an analogous character, whose constitution is likely to be illustrated by this line of researches. The basic substances derived from aniline, when expressed in formulæ excluding any peculiar view respecting the mode in which the elements are arranged, present a series which is exhibited in the following synoptical table:—

Aniline . . . . .	$C_{12} H_7 N =$
Methylaniline . . . . .	$C_{14} H_9 N = C_{12} H_7 N + C_2 H_2$
Ethylaniline . . . . .	$C_{16} H_{11} N = C_{12} H_7 N + 2 C_2 H_2$
Methylethylaniline . . . . .	$C_{18} H_{13} N = C_{12} H_7 N + 3 C_2 H_2$
Diethylaniline . . . . .	$C_{20} H_{15} N = C_{12} H_7 N + 4 C_2 H_2$
Amylaniline . . . . .	$C_{22} H_{17} N = C_{12} H_7 N + 5 C_2 H_2$
Ethylamylaniline . . . . .	$C_{26} H_{21} N = C_{12} H_7 N + 7 C_2 H_2$
Diamylaniline . . . . .	$C_{32} H_{27} N = C_{12} H_7 N + 10 C_2 H_2$

This table shows that the alkaloids in question differ from each other by  $n C_2 H_2$ , the elementary difference of the various alcohols and their derivatives; we perceive moreover that the series ascends regularly up to the term  $C_{12} H_7 N + 5 C_2 H_2$ , when the compound  $C_{12} H_7 N + 6 C_2 H_2$  is wanting; lastly, we miss the terms  $C_{12} H_7 N + 8 C_2 H_2$  and  $C_{12} H_7 N + 9 C_2 H_2$ . The first gap might be easily filled by submitting amylaniline to the action of iodide of methyl, methylamylaniline being in fact  $C_{24} H_{19} N = C_{12} H_7 N + 6 C_2 H_2$ . The other wanting terms cannot be reached from aniline before some of the missing alcohols are discovered.

\* Chem. Soc. Quart. Journ. ii. p. 331.



On examining more closely the formulæ of the preceding conspectus, we find that several of them represent basic compounds previously known. Chemists are acquainted with the beautiful reaction by which ZININ first linked aniline to benzole through nitrobenzole.



Researches performed in the most different departments of organic chemistry have gradually elicited a series of carbohydrides differing from benzole by  $n \text{C}_2 \text{H}_2$ , and each of these terms, when treated with nitric acid, and subsequently exposed to the action of reducing agents, has yielded its corresponding base. We are now in the possession of the following series of alkaloids derived from hydrocarbons:—

Benzole	$\text{C}_{12} \text{H}_6$	Aniline	$\text{C}_{12} \text{H}_7 \text{N}$
Toluole	$\text{C}_{14} \text{H}_8 = \text{C}_{12} \text{H}_6 + \text{C}_2 \text{H}_2$	Toluidine	$\text{C}_{14} \text{H}_9 \text{N} = \text{C}_{12} \text{H}_7 \text{N} + \text{C}_2 \text{H}_2$
Xylole	$\text{C}_{16} \text{H}_{10} = \text{C}_{12} \text{H}_6 + 2 \text{C}_2 \text{H}_2$	Xylidine*	$\text{C}_{16} \text{H}_{11} \text{N} = \text{C}_{12} \text{H}_7 \text{N} + 2 \text{C}_2 \text{H}_2$
Cumole	$\text{C}_{18} \text{H}_{12} = \text{C}_{12} \text{H}_6 + 3 \text{C}_2 \text{H}_2$	Cumidine†	$\text{C}_{18} \text{H}_{13} \text{N} = \text{C}_{12} \text{H}_7 \text{N} + 3 \text{C}_2 \text{H}_2$
Cymole	$\text{C}_{20} \text{H}_{14} = \text{C}_{12} \text{H}_6 + 4 \text{C}_2 \text{H}_2$	Cymidine‡	$\text{C}_{20} \text{H}_{15} \text{N} = \text{C}_{12} \text{H}_7 \text{N} + 4 \text{C}_2 \text{H}_2$

On comparing the formulæ of the bases contained in the last table with those representing the alkaloids derived from aniline by the introduction of methyl and ethyl, we find that they exactly coincide. Toluidine has the same composition as methylaniline; xylidine, cumidine and cymidine are represented by the same formulæ as ethylaniline, methylethylaniline and diethylaniline. The question then arises, are these substances identical, or are they only isomeric with each other? I have carefully compared the properties of toluidine with those of methylaniline, and also methylethylaniline with cumidine. These substances are not identical, but only isomeric. The most striking dissimilarity we observe in the characters of toluidine and methylaniline. The former is a beautiful crystalline compound, boiling at  $198^\circ$ , yielding difficultly soluble, perfectly stable salts with almost all acids, and a splendid orange-yellow platinum-salt, which may be boiled without decomposition. We are unacquainted with any process by which we could convert this body into aniline. Methylaniline, on the other hand, is an oily liquid, boiling at  $192^\circ$ , whose salts are distinguished by their solubility and by the facility with which they are decomposed, aniline being reproduced (*vide* p. 113). The platinum-salt, even when freshly precipitated, is of a pale-yellow colour, which immediately darkens, turning perfectly black after the lapse of an hour. Scarcely less striking is the dissimilarity of cumidine and methylethylaniline, although in this case both substances are liquids. For

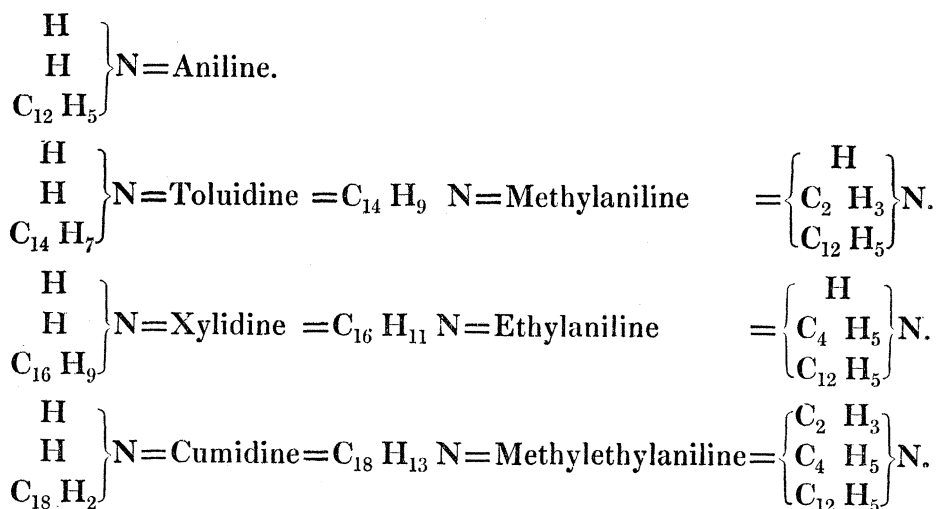
\* Unpublished researches of M. CAHOUS. This chemist has lately found the long-wanted carbohydride  $\text{C}_{16} \text{H}_{10}$ , among the products of the distillation of wood. It comports itself exactly like benzole and its congeners, yielding nitroxylole and xylidine.

† On Cumidine, a new Organic Base, by E. CHAMBERS NICHOLSON, Chem. Soc. Quart. Journ. i. 1.

‡ This compound has been partly investigated by Mr. NOAD.

details I refer to Mr. NICHOLSON's\* paper on Cumidine, and to what I have stated about methylethylaniline (*vide* p. 114). The quantity of this substance I had at my disposal was not sufficient for a determination of the boiling-point; but if we recollect that ethylaniline boils at  $204^{\circ}$ , and that the introduction of methyl into aniline raised its boiling-point about  $10^{\circ}$ , it is evident that methylethylaniline cannot boil at a temperature much higher than  $214^{\circ}$ , *i. e.* eleven degrees below  $225^{\circ}$ , the boiling-point of cumidine observed by Mr. NICHOLSON. An account of the properties of xylidine has not yet been published; however, I have not the slightest doubt that M. CAHOURS will find them widely differing from those of ethylaniline.

Toluidine, xylidine and cumidine, resembling aniline, not only in their physical characters, but also in their origin from carbohydrides, evidently belong to the class of alkaloids for which I have provisionally retained the name amidogen-bases, while the basic compounds derived from aniline are either imidogen- or nitrile-bases. The difference of properties depends upon a difference in the molecular construction, as represented graphically by the following table:—

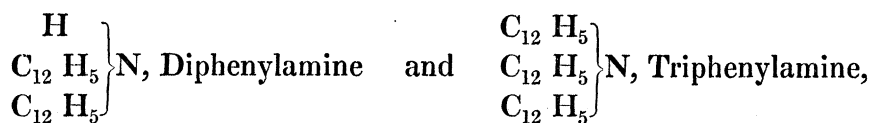


These formulæ assume the existence of a series of homologous radicals of compounds resembling in their chemical deportment, to a certain extent, the alcohols of the series  $\text{C}_n\text{H}_{n+2}\text{O}_2$ . In a former paper†, I have shown how this resemblance becomes more and more marked with every new investigation performed in this department of the science. A judicious application to these substances of the various methods hitherto employed in combining the radicals of the common alcohols with bromine or iodine, will probably enable us before long to obtain the corresponding products in the phenyl-, toluyl-, xyl- and cumyl-series. The discovery of these substances will furnish us at once with new processes for the production of the basic compounds in question, for it cannot be doubted that their action upon ammonia will give rise to the formation of the respective alkaloids with the same facility with which the treatment of ammonia with bromide and iodide of ethyl induces the form-

\* *Loc. cit.* p. 125.

† Chem. Soc. Quart. Journ. ii. p. 329.

ation of ethylamine; we may hope moreover to form the imidogen- and nitrile-terms of these radicals, in the phenyl-series for instance :—

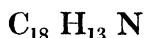


the production of which, as mentioned in the commencement of this paper, I have in vain attempted by the action of the phenyl-alcohol at high temperatures upon aniline.

The view which I propose in the preceding remarks respecting the constitution of toluidine, xyloidine and cumidine, must as yet be considered as a mere hypothesis. It will not however be difficult to establish it by facts. The action of bromide of ethyl upon these substances will at once decide this question. These bases, when subjected to the influence of the bromides, will give rise to the formation of a series of bases similar to those which I have obtained from aniline. I may mention that the deportment of toluidine and cumidine, in this respect, is now being studied by several of my pupils. There is no difficulty in introducing 1 equiv. of ethyl into toluidine; the experiments are however not yet sufficiently advanced as to affirm also the insertion of the second equivalent. The alkaloid obtained by acting with bromide of ethyl upon toluidine is represented by the formula

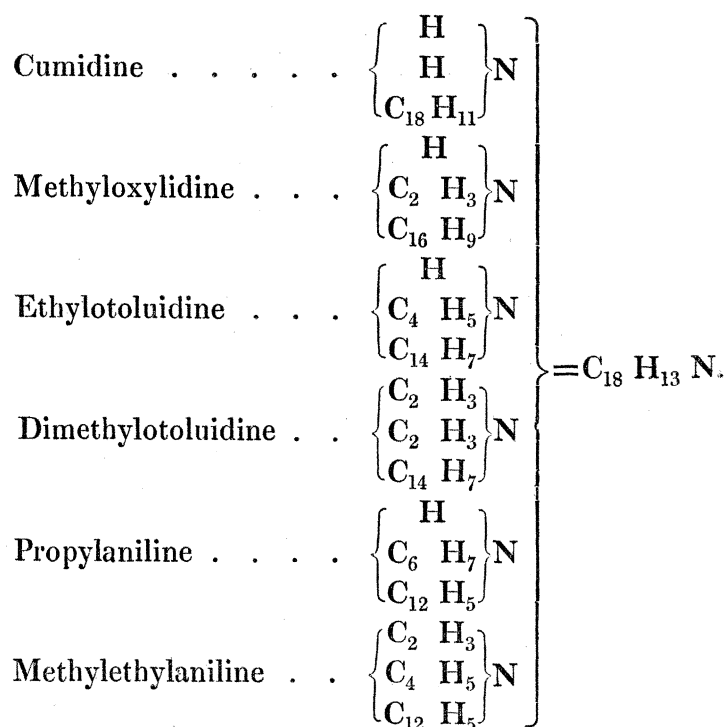


so that we are now in possession of three alkaloids of exactly the same composition, namely, ethyltoluidine, methylethylaniline and cumidine; and here I cannot but allude to the wonderful variety of isomeric compounds to which a continuation of these researches must necessarily lead. We see at a glance that substances of the formula



will also be obtained by inserting 1 equiv. of methyl into xyloidine, by introducing 2 equivs. of methyl into toluidine, or by fixing upon aniline the radical (propyl) belonging to the missing alcohol of propionic acid\* (metacetic acid). We thus arrive at six alkaloids, having all the same numerical formulæ, but widely differing in their construction.

\* A more appropriate name for metacetic acid, proposed by DUMAS, MALAGUTI and LEBLANC (Compt. Rend. xxv. 656), as it is the *first* acid of the series  $\text{C}_n \text{H}_n \text{O}_4$  that exhibits the character of a *fatty* acid, *i. e.* in being separated from solution as a layer of oil, and in forming salts with the alkalies that have a greasy appearance.

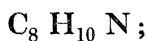


This multiplicity of course augments in the same measure as we ascend upon the scale of organic compounds. For every step the number of possible isomeric bases increases by two, so that on arriving at the term diamylaniline,



being the last member (*vide* p. 124) in the aniline-series which I have examined, we find that its numerical formula actually represents not less than twenty different alkaloids which the progress of science cannot fail to call into existence,—a striking illustration of the simplicity in variety that characterizes the creations of organic chemistry.

Not less numerous will be the isomerisms in the series of bases derived by the insertion into ammonia of the alcohol-radicals  $\text{C}_n \text{H}_{n+1}$  only, as soon as the group of these alcohols themselves shall be more completely known. Ethylamine is isomeric with dimethylamine; diethylamine has the same composition as methylopropylamine, a base containing ethyl and propyl, the alcohol-radical in the propionic (metacetic) series, as dimethylethylamine, and lastly, as butylamine. Some chemists are actually inclined to consider as such a volatile alkaloid discovered by Dr. ANDERSON\* among the products of the distillation of animal substances, and described by him under the name of petinine. The formula established by Dr. ANDERSON is



but it is not unlikely that on repeating the analysis an additional hydrogen-equivalent

\* Transactions of the Royal Society of Edinburgh, xvi. 4.

will be found. The boiling-point of the compound ( $75^{\circ}$ ) is very much in favour of butylamine\*.

In a similar manner a great number of bases identical in composition with triethylamine will soon be found; capronamine, methylamylamine, ethylobutylamine, dipropylamine, and a number of others.

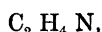
In concluding this paper, which, from the great number of experimental details which I had to bring forward, has been swelled almost beyond legitimate dimensions, I cannot but allude to the aid which the study of the natural alkaloids may possibly derive from a prosecution of these researches. I am, as I have said, far from believing that the constitution of substances, like quinine and morphine, is as simple as that of the bases described in the preceding memoir; we know that the typical system



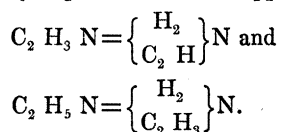
may in a variety of ways assimilate several other groups of elements without forfeiting its original character. Cyaniline, melaniline† and dicyanomelaniline, and their

\* A perfectly similar remark applies to a compound lately discovered by ROCHLEDER among the products of decomposition of caffeine (Ann. Chem. und Pharm. lxxi. 7), and described by him under the name of formyline.

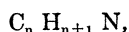
The formula



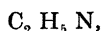
which ROCHLEDER gives for this compound, is, after we have become acquainted with the mode in which the methyl- and ethyl-bases are produced, very improbable. There appears to me a choice only between the formulæ



The former of these formulæ is improbable, on account of the great discrepancy both in the hydrogen and platinum observed and calculated; and it may be mentioned here that the existence of a series of bases of the formula



i. e. bases containing formyl, acetyl, propionyl (metacetyl), butyryl, &c., appears to be still doubtful on account of the electro-negative character of these radicals. By the action of bromide of acetyl,  $C_4 H_3 Br$ , upon ammonia, I have not as yet been able to obtain an alkaloid. The formula



which is that of methylamine, discovered by M. WURTZ, has analogy in its favour. The slight deficiency in the hydrogen can, it would appear, be scarcely adduced in opposition to the formulæ. The three formulæ are represented by the following numbers, which I place in juxtaposition with the mean of the analytical results.

	$C_2 H_3 N.$	$C_2 H_4 N.$	$C_2 H_5 N.$	Mean of analysis.
Carbon .....	5.10	5.09	5.06	4.86
Hydrogen.....	1.70	2.12	2.53	2.45
Platinum .....	42.52	41.77	41.60	41.39

† It seems that the homologues of aniline yield derivatives with the same facility as aniline itself: Mr. WILSON is at present engaged in studying the action of chloride of cyanogen upon toluidine; he has obtained a beautiful alkaloid represented by the formula  $C_{30} H_{17} N_3$ , which corresponds to melaniline.

congeners, are well-marked instances of such increasing complexity. The constitution of the natural alkaloids may be still more intricate. However, a series of well-devised experiments will not fail to exhibit the framework of these substances, an inspection of which will enable us to reconstruct them with the same facility as we build up our series of alcohol-bases.

The powerful and defined action of bromide of ethyl which I have pointed out in this paper will, it would appear, materially assist in the solution of this problem. We might by its aid succeed in ascertaining the state of substitution in which the ammonia exists in these compounds, or in other words, whether the alkaloid in question is an amidogen-, imidogen-, or nitrile-base. Some preliminary experiments made with two natural alkaloids, with nicotine and coniine, more closely allied, it is true, with the aniline-group than quinine, &c., appear to promise a harvest of interesting results. These substances evidently contain still basic hydrogen, for on mixing them with bromide of ethyl, they are rapidly attacked, with formation of the hydrobromates of two new bases, of which the salt of the nicotine-derivative is obtained in large beautiful crystals. An extension of this study to the bases of the cinchona bark and of opium, and to the bases of the series  $C_n H_{n+1} N O_4$  (glycocine, sarcosine, leucine, &c.), whose constitution is at present still very enigmatical, may perhaps lead to similar results. These substances, complicated as their construction may appear at the first glance, will perhaps be found of a surprising simplicity when subjected to a closer examination. I may here quote the curious results which various chemists have obtained by treating with nitric acid and other powerful agents several of the natural alkaloids, results from which it would almost appear that several of these alkaloids, brucine and narcotine for instance, do actually contain methyl or ethyl, inasmuch as their decomposition seems to give rise to the formation of compounds of these radicals. The presence of such radicals as methyl and ethyl in natural alkaloids, is in itself scarcely a startling fact. We are still perfectly in the dark as to whether the pyroxylic spirit which we obtain in the dry distillation of wood is actually a product of destructive distillation, or whether it pre-existed in the wood before the process. At all events we know from the splendid researches of M. CAHOURS on the oil of *Gaultheria procumbens*, that methyl-compounds are actually secreted in the organism of plants. Ammonia in a nascent state coming into contact with these and other compounds, might easily give rise to the formation of basic substitution-products. In a recent communication, Dr. STENHOUSE\* has proved that whenever ammonia separates from nitrogenous organic matter, by dry distillation, putrefaction, &c., we have invariably a formation of organic bases attending the evolution of this compound.

However, the question as to whether brucine and narcotine actually yield alcoholic compounds being still *sub judice*, it is better to defer for the present any farther speculations which might present themselves.

\* Transactions of the Royal Society for 1850, Art. II. p. 56.

In conclusion, I append a synoptical view of the various basic compounds which I have derived from ammonia; this will exhibit the chief results of these researches, better perhaps than would a brief recapitulation of the several facts.

TYPE.	AMIDOGEN-BASES.		IMIDOGEN-BASES.		NITRILE-BASES.		
Ammonia (Amine)	Aniline (Phenylamine)	$\left\{ \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12} \text{ H}_5 \end{array} \right\} \text{N.}$	Ethylaniline (Ethylophenylamine)	$\left\{ \begin{array}{c} \text{H} \\ \text{C}_4 \text{ H}_5 \\ \text{C}_{12} \text{ H}_5 \end{array} \right\} \text{N.}$	Diethylaniline (Diethylophenylamine)	$\left\{ \begin{array}{c} \text{C}_4 \text{ H}_5 \\ \text{C}_4 \text{ H}_5 \\ \text{C}_{12} \text{ H}_5 \end{array} \right\} \text{N.}$	
			Methylaniline (Methylophenylamine)	$\left\{ \begin{array}{c} \text{H} \\ \text{C}_2 \text{ H}_3 \\ \text{C}_{12} \text{ H}_5 \end{array} \right\} \text{N.}$	Methylethylaniline (Methylethylophenylamine)	$\left\{ \begin{array}{c} \text{C}_2 \text{ H}_2 \\ \text{C}_4 \text{ H}_5 \\ \text{C}_{12} \text{ H}_5 \end{array} \right\} \text{N.}$	
			Amylaniline (Amylophenylamine)	$\left\{ \begin{array}{c} \text{H} \\ \text{C}_{10} \text{ H}_{11} \\ \text{C}_{12} \text{ H}_5 \end{array} \right\} \text{N.}$	Diamylaniline (Diamylophenylamine)	$\left\{ \begin{array}{c} \text{C}_{10} \text{ H}_{11} \\ \text{C}_{10} \text{ H}_4 \\ \text{C}_{12} \text{ H}_5 \end{array} \right\} \text{N.}$	
	Chloraniline (Chlorophenylamine)	$\left\{ \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12} \left( \text{H}_4 \right) \\ \text{Cl} \end{array} \right\} \text{N.}$	Ethylochloraniline (Ethylochlorophenylamine)	$\left\{ \begin{array}{c} \text{H} \\ \text{C}_4 \text{ H}_5 \\ \text{C}_{12} \left( \text{H}_4 \right) \\ \text{Cl} \end{array} \right\} \text{N.}$	Diethylochloraniline (Diethylochlorophenylamine)	$\left\{ \begin{array}{c} \text{C}_4 \text{ H}_5 \\ \text{C}_4 \text{ H}_5 \\ \text{C}_{12} \left( \text{H}_4 \right) \\ \text{Cl} \end{array} \right\} \text{N.}$	
			Bromaniline (Bromophenylamine)	$\left\{ \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12} \left( \text{H}_4 \right) \\ \text{Br} \end{array} \right\} \text{N.}$	Ethylbromaniline (Ethylbromophenylamine)	$\left\{ \begin{array}{c} \text{H} \\ \text{C}_4 \text{ H}_5 \\ \text{C}_{12} \left( \text{H}_4 \right) \\ \text{Br} \end{array} \right\} \text{N.}$	
			Nitraniline (Nitrophenylamine)	$\left\{ \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12} \left( \text{H}_4 \right) \\ \text{NO}_4 \end{array} \right\} \text{N.}$	Ethylonitraniline (Ethylonitrophenylamine)	$\left\{ \begin{array}{c} \text{H} \\ \text{C}_4 \text{ H}_5 \\ \text{C}_{12} \left( \text{H}_4 \right) \\ \text{NO}_4 \end{array} \right\} \text{N.}$	
	Ethylamine (Ethylammonia)	$\left\{ \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_4 \text{ H}_5 \end{array} \right\} \text{N.}$	Diethylamine (Diethylammonia)	$\left\{ \begin{array}{c} \text{H} \\ \text{C}_4 \text{ H}_5 \\ \text{C}_4 \text{ H}_5 \end{array} \right\} \text{N.}$	Triethylamine (Triethylammonia)	$\left\{ \begin{array}{c} \text{C}_4 \text{ H}_5 \\ \text{C}_4 \text{ H}_5 \\ \text{C}_4 \text{ H}_5 \end{array} \right\} \text{N.}$	