

ART. VII.—*On Triethylamine*; by M. CAREY LEA, Philadelphia.

THE triethylamine which served for the following examinations was obtained, by the action of nitrate of ethyl upon ammonia, making the alkaloids thus obtained react upon fresh portions of the compound ether. The following was the course of the operation.

Three volumes of nitrate of ethyl with three volumes of liquid ammonia, thoroughly saturated with ammoniacal gas and two volumes of absolute or nearly absolute alcohol, were sealed up in glass tubes and were kept in boiling water for four hours. The tubes were then opened, the contents neutralized with nitric acid, and evaporated over a chlorid of calcium bath. When freed as far as possible from water, the pasty mass was placed in a flask, with four volumes of absolute or nearly absolute alcohol and a sufficient quantity of caustic soda in powder. Heat was applied and the vapors disengaged were conducted into three volumes of nitrate of ethyl mixed with two of absolute alcohol, kept cool by a freezing mixture. At the close of the operation it was necessary to add a little water to the contents of the flask in order to complete the decomposition. The absorption of the distillate was complete, and the liquid thus saturated was again enclosed in sealed tubes and heated. The entire number of charges was forty-two, of which five were lost by explosion. For the convenience of those who may use this method of obtaining the ethyl bases, I give the results which I observed as to the strength of tube necessary :

Tubes of one inch external diameter, weighing	
5 ounces to the foot generally burst.	
6 to 7 “ “	generally resisted, but not always.
8 to 10 “ “	were found safe.

This refers to tubes charged from three-sevenths to one-half. Beyond this charge, greatly increased strength becomes necessary.*

The disposition to burst appeared to be greater in the second heating than in the first. It is therefore better to heat for 11 or 12 hours to 180°–190° F. rather than risk the loss of products which have already cost considerable time and trouble.

In describing the properties of ethylamine and diethylamine, I have shown that when nitrate of ethyl is made to react upon ammonia, the resulting alkaloids are easily separated from each other by means of picric acid. It is a familiar fact that when several salts are present in one solution, the facility of separating them by crystallization will often depend upon the relative proportion in which they are present, and this holds good in the present case. When ammonia acts upon nitrate of ethyl, and the bases, after separating the ammonia, are converted into picrates, we have a mixture of the salts of ethylamine and diethylamine in nearly equal quantities, with a variable quantity of triethylamine, always very small and sometimes a mere trace, always separating out in the first crystallization. But when nitrate of ethyl is made to react again upon the products of the first reaction, the proportions of the alkaloids are very different. Diethylamine then constitutes about three-fourths of the whole, and the residue is chiefly triethylamine mixed with some ethylamine. When these bases are converted into picrates the diethylamine salt still separates with great facility, sinking to the bottom at a certain stage of concentration as a heavy oily fluid.† Previously to this,

* It has been very generally recommended in text books to wrap pressure tubes in cloths to prevent the explosion of one from destroying the rest. When this is done, the extremities of the tube should always be left clear. It is at the extremity that the explosion almost always takes place, and if there is not an easy escape for the expanding vapors, so great a disturbance follows that much damage may be done. In this way I have seen every tube in a boiler broken by the explosion of one, whereas, since I have adopted the plan of leaving the ends perfectly free, when an accident has taken place I have always escaped with the loss of the one.

† The latter portions of this oily fluid which separate are often pasty with the needles of the less soluble compounds, from which they are best separated by ether in which picrate of diethylamine is extremely, and the other picrates very sparingly soluble. As a proof how exactly diethylamine may be separated from its cognate bases by conversion into picrates, I subjoin analyses made at various times, some of which have been published before, others not:

(1.)	7144 gramms chloroplatinate gave Pt,	2552
(2.)	9961 " " "	3549
(3.)	3884 " " "	1377
(4.)	19129 " " "	6764

These correspond to

(1.)	Per cent platinum,	-	-	-	-	35.72
(2.)	" "	-	-	-	-	35.63
(3.)	" "	-	-	-	-	35.45
(4.)	" "	-	-	-	-	35.36
	Theory requires (Pt=98.7)	-	-	-	-	35.35
	" " (Pt=99)	-	-	-	-	35.45

the picrates of ethylamine and triethylamine crystallize out in yellow needles. The separation of these last from each other by crystallization when the triethylamine is present in considerable proportion, cannot be as satisfactorily effected, as when it is present in small quantity only. It therefore became necessary to seek for a good mode of effecting this separation.

Triethylamine is but moderately soluble in water, and when the water present is insufficient to dissolve it, it forms a layer on the surface. It seemed possible that its affinity for ether might be greater than for water, and experiment proved this to be the case. When ether is agitated with aqueous solution of ammonia, ethylamine, or diethylamine, it takes up but little of the base, but when agitated with aqueous solution of triethylamine, it becomes strongly charged. A portion of ether agitated with a mixture of the aqueous solutions of ethylamine and triethylamine and then treated with hydrochloric acid and bichlorid of platinum and spontaneously evaporated, gave only crystals of triethylamine salt, which is easily distinguished from the platinum salt of ethylamine: no traces of the presence of the latter were observable. It therefore seemed worth while to test the process by a careful series of analyses, which was done with the following results.

The moderately strong aqueous solution of the mixed bases, triethylamine and ethylamine, was agitated several times with about $\frac{1}{16}$ its bulk of ether and left some time to separate thoroughly, after which the ether was removed by a separating funnel. This was repeated three or four times. It was evident that if these ethereal solutions of triethylamine thus obtained were contaminated with ethylamine, the latter substance would be present in largest proportion in the latter portions of the ether. In order therefore to render the test more rigorous, these latter were examined in preference, and with the following results.

Portions of the ethereal solution were treated with excess of hydrochloric acid and converted into platinum salt with excess of bichlorid of platinum.

(1.)	·7031	gms. substance gave metallic platinum,	·2264
(2.)	1·2084.	“ “ “ “	·3873
These correspond to			
(1.)	per cent platinum,	- - - - -	32·20
(2.)	“ “	- - - - -	32·06
Mean of two analyses, - - - - -			32·13
Theory requires (Pt=98·7)* - - - - -			32·13

An eminently satisfactory result.

In order to ascertain if the whole of the triethylamine were removed by this proceeding, the aqueous solution, after four washings with ether, was submitted to analysis. Its chloroplatinate gave by ignition

* I have taken this number for Pt as that adopted by the last numbers of the *Jahresbericht*.

·6373 substance, platinum, - - - - -	·2487
Corresponding to, per cent platinum, - - - - -	39·02
Theory requires, - - - - -	39·29

The number found falls a little below the theoretical proportion, and may indicate that a trace of triethylamine remained in the aqueous solution. I may however remark that this slight discrepancy is within the error of a careful analysis, particularly with substances whose analysis requires so much circumspection as these. Two analyses of chloroplatinate of ethylamine of which the alkaloid had been separated by picric acid gave respectively 39·02 and 39·23, the first of which numbers is identical with that above found.

Ether appears therefore to afford a convenient mode of separating ethylamine and triethylamine, after diethylamine has been eliminated by means of picric acid. This is a necessary condition: when observed, the process gives, so far as my experiments go, good results.

Properties of Triethylamine.

Triethylamine is an oily fluid lighter than water, and floating on its surface when the water present is insufficient in quantity to hold it in solution. When therefore the crystallized hydrochlorate is added to a concentrated solution of caustic soda, the triethylamine separates and rises to the surface. It has an agreeable ammoniacal odor, which appeared to me to be pleasanter and more aromatic than those of ethylamine and diethylamine. This however is a matter on which it is difficult to speak positively, as the odor of ammonias appears to be influenced by adventitious circumstances. Stas found the odor of perfectly pure ammonia prepared by him, to be quite different from that ordinarily recognized as characteristic of the substance.

It is not very soluble in water, but emulsifies very easily with it. When a stratum of triethylamine is resting upon the surface of a saturated aqueous solution, a very slight agitation is sufficient to produce a complete emulsion, and a considerable time elapses before the stratum separates again. It is capable of acting under some circumstances as a reducing agent, separating gold in the metallic state with production of aldehyd, as will be described further on, but unites with chromic acid without decomposition.

Reactions of Triethylamine with solutions of metallic bases.

The following reactions were obtained with a saturated aqueous solution of pure triethylamine:

Zirconium, sulphate of Zirconia,	White precipitate, insoluble in excess of precipitant.
Aluminium, tersulphate alumina,	White precipitate, dissolving readily and completely in excess of the precipitant.

Glucinum, sulphate of glucina,	White precipitate, insoluble in excess of precipitant.
Cadmium, sulphate,	White precipitate, insoluble in excess of precipitant.
Zinc, sulphate,	Same reaction.
Nickel, chlorid,	Green precipitate, insoluble in excess of precipitant.
Cobalt, protochlorid,	Greenish blue precipitate, insoluble in excess of precipitant.
Lead, neut. acetate,	The white precipitate dissolves in excess of lead solution, but is insoluble in any excess of triethylamine.
Tin, protochlorid,	White precipitate, insoluble in excess of precipitant.
“ bichlorid,	White precipitate, dissolving completely in excess of precipitant.
Silver, nitrate,	Brown precipitate, somewhat soluble in excess of precipitant.
Gold, terchlorid,	Yellow precipitate, insoluble in excess and speedily becoming blackish.
	The action of triethylamine on gold solution is remarkable and may be considered as the most distinctive characteristic between this and the allied alkaloids. Triethylamine added to terchlorid of gold throws down a yellow precipitate, which in a few moments darkens and soon appears black, but examined in thin layers is found to be dark bluish green. This precipitate treated with hydrochloric acid partly dissolves with formation of terchlorid and leaves a residue of metallic gold in the form of a brown powder. The precipitate at first formed by the alkaloid speedily passes therefore into protoxyd of gold. This reduction is accompanied by the evolution of aldehyd, and is carried even further than the production of protoxyd, part of the gold being reduced to the metallic form. For after standing a few minutes, a bright film of gold collects on the surface of the liquid, and after a few hours the sides of the test glass are found to be covered with a brilliant speculum of metallic gold.
Platinum, protochlorid,	No precipitate.
“ bichlorid,	A saturated aqueous solution of triethylamine gives no precipitate with a concentrated solution of bichlorid of platinum.

Palladium, protochlorid,	No precipitate.
Ruthenium, sesquichlorid,	No immediate precipitate. The liquid however soon begins to darken, and a black precipitate falls, which gradually increases until the liquid is decolorized.
Antimony, terchlorid,	Reddish brown precipitate.
Uranium, nitrate,	Abundant yellow crystalline precipitate, insoluble in excess of precipitant.
Mercury, ternitrate,	Yellowish white precipitate, insoluble in excess.
Molybdenum, protochlorid,	Becomes opalescent and by standing deposits a yellowish powder.*
“ bichlorid,	Brownish yellow precipitate, insoluble in excess of precipitant.
Chromium, potash chrome alum,	Greyish green precipitate, insoluble in excess of precipitant.
Iron, ferric ammonia alum,	Brown, insoluble in excess.
Copper, sulphate,	Blue precipitate of which not a trace redissolves in excess of the alkaloid. The precipitate after treatment with a large excess of saturated aqueous solution of triethylamine, was filtered and the filtrate tested with sulphhydrate of ammonia, which gave not the slightest indication of the presence of copper.
Manganese, protosulphate,	Brownish white, insoluble in excess of precipitant.
Magnesia, sulphate,	White precipitate, insoluble in excess.
Cerium, protochlorid,	White precipitate, insoluble in excess of the precipitant.
“ nitrate of protoperoxyd,	Same reaction.

Reactions with Hydrofluosilicic Acids.

Aqueous triethylamine treated with ordinary hydrofluosilicic acid, HF_3 , SiF_6 , gives, when the alkaloid is in excess, a precipitate which readily dissolves in an excess of the acid.

With Knop's hydrofluosilicic acid 2HF_3 , Si_2F_7 , no immediate precipitate is formed even when the alkaloid is in excess, but after standing some hours, it becomes a slightly opalescent but almost transparent jelly, so stiff that the test glass may be inverted without spilling it.

Observations on these Reactions—I have already pointed out that the property of redissolving precipitates of alumina, heretofore considered as characteristic of ethylamine, is shared by both diethylamine and methylamine, and expressed the opinion

* Methylamine also precipitates solutions of this salt. My correction of the contrary statement in the last number of this Journal (p. 369) reached the editors when the impression was too far advanced to alter it.

that it might probably be found to extend to the other ethyl and methyl bases. The result above stated affords a confirmation of this view as regards the base now under examination.

The most important points deducible from the above described reactions may be summed up as follows: Towards solution of aluminium, cadmium, nickel, protochlorid of cobalt and bichlorid of tin, the behavior of triethylamine is the same as that of ethylamine and diethylamine, and differs from that of ammonia. With respect to zinc, the behavior of triethylamine resembles that of diethylamine and differs from that of both ammonia and ethylamine. In speaking of the reactions of diethylamine, I pointed out that the oxyds of silver and copper were the only ones redissolved by all three bases, ammonia, ethylamine and diethylamine. We now see that only one, silver, is dissolved by all four, including that here investigated.

Extending the comparison to methylamine and denoting by (W.), reactions observed and recorded by its discoverer, M. Wurtz, with respect to that substance, we find that gold precipitates redissolve in excess of methylamine, but not in excess of triethylamine. Protochlorid of palladium is precipitated by methylamine, and not by triethylamine. Alumina is precipitated and redissolved by both. Zinc, silver, and copper precipitates are redissolved by excess of methylamine (W.) but are insoluble in triethylamine. With respect to cadmium, nickel, and cobalt, the precipitates from solutions of these metals are insoluble in methylamine (W.) and in triethylamine.

Finally we observe that those reactions which may be considered as being eminently characteristic of triethylamine, are those which it exhibits with gold and with copper. These and these only, differ essentially from the reactions of ammonia, ethylamine, diethylamine and methylamine respectively. That with gold solution is especially interesting.

Salts of Triethylamine.

Hydrochlorate.—Crystallizes with great facility in beautiful snow-white feathery laminae. It is not in the least deliquescent in tolerably dry air;—a portion left exposed for several days in a watch glass did not exhibit the least tendency to liquify. Carefully heated on platinum foil, it disappears without leaving any carbonaceous residue.

The most curious property of this salt is its easy combustibility. A portion of the dry salt readily ignites by contact with a lighted match and burns with a livid green flame.

Sulphate.—Very soluble in water and alcohol. Exposed over lumps of caustic soda, in vacuo, for some weeks, it solidifies to an indistinctly crystalline mass. Heated on platinum foil, it takes fire and burns with a scarcely luminous flame and yellowish scintillations.

Nitrate.—The nitrate of triethylamine appears to be liquid at ordinary temperatures, and is obtained by neutralizing aqueous triethylamine with nitric acid, gently evaporating at a low temperature until the solution is somewhat concentrated, and then placing in vacuo over caustic soda for some weeks. A thick syrupy liquid is thus obtained which does not crystallize. When filtering paper is imbued with this liquid and brought near to a flame, it deflagrates with a sudden flash.

A double sulphate of zinc and triethylamine isomorphous with the double sulphates of Mitscherlich's group does not appear to exist.