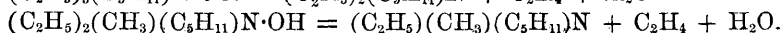
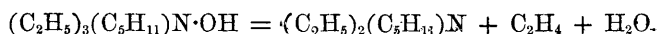


LIII.—*The Action of Heat on the Chlorides and Hydroxides of Mixed Quaternary Ammonium Compounds.*

By N. COLLIE, Ph.D., and S. B. SCHRYVER, B.Sc.

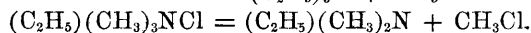
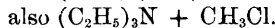
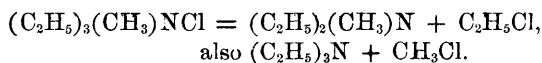
THE object of the following work was to obtain, if possible, a general method for preparing the mixed tertiary amines. One of us (Collie, *Trans.*, 1888, 714—726) has found that by the action of heat upon the quaternary phosphonium compounds various mixed tertiary phosphines could be prepared, and the following results show distinctly a marked analogy between the compounds of nitrogen and those of phosphorus.

Hofmann has already pointed out that when the hydroxides of mixed quaternary ammonium compounds containing ethyl-groups are heated, invariably one of the ethyl-groups is eliminated in the form of ethylene (Hofmann, *Annalen*, **78**, 282—284, and **79**, 12—15):—



And Lossen (*Annalen*, **81**, 376—383) confirms the results of Hofmann with regard to the action of heat on the mixed ethylmethylammonium hydroxides.

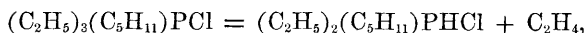
He has also tried the action of heat on some of the corresponding chlorides with the following results:—



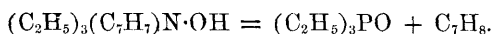
But none of the mixed tertiary amines thus prepared was obtained in the pure state; both Hofmann and Lossen being content to convert them back again into quaternary ammonium compounds, and analyse the platinum salts.

There was therefore, no doubt that mixed tertiary amines could be prepared both from the hydroxides and chlorides of the mixed quaternary ammonium compounds, and a wider field for investigation was opened with the ammonium compounds than with the corre-

sponding phosphonium-derivatives. For the quaternary phosphonium chlorides alone yielded mixed tertiary phosphines when decomposed by heat:—



whilst the hydroxides, owing to the great affinity of phosphorus for oxygen, always gave tertiary phosphine oxides:—



In the present work, we have always used as a starting point either trimethylamine or triethylamine, and from these tertiary amines we have prepared the quaternary ammonium compounds by heating an alcoholic solution of the amine with the iodide or chloride of primary, secondary, or tertiary hydrocarbon radicles of the $\text{C}_n\text{H}_{2n+1}$ series. The action of heat on the quaternary ammonium compounds containing the radicles allyl, benzyl, and phenyl has also been studied.

The trimethylamine and triethylamine were prepared by the action of heat on tetramethylammonium and tereethylammonium chlorides; these salts decompose quantitatively when heated as follows:—

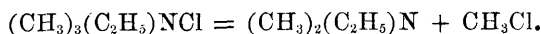


The free amine was collected in hydrochloric acid, and the hydrochlorides thus obtained were concentrated to the consistency of a syrup. Portions of the salt were decomposed from time to time with saturated caustic soda solution, and the free tertiary amine distilled into dry alcohol.

I.—MIXED QUATERNARY AMMONIUM COMPOUNDS PRODUCED FROM TRIMETHYLAMINE.

The Action of Heat on Trimethylethylammonium Chloride.

This salt was prepared from a strong alcoholic solution of trimethylamine by adding ethyl iodide, and converting the iodide thus formed into the chloride. An analysis of the iodide was made (iodine found 59.1 and 53.9 per cent.; theoretical iodine = 59.0 per cent.). A small quantity of the chloride was also converted into the platinum salt and analysed (platinum found 33.1 per cent.; theoretical, 33.3 per cent. Pt). The action of heat on this mixed chloride has already been tried by Lossen, who found that it decomposed as follows:—



We were, however, anxious to obtain, if possible, the mixed tertiary amine pure, and so repeated his experiment.

A preliminary experiment was first tried with 4.3 grams of the solid chloride. At a temperature above 300° the salt decomposed without fusion. The products were passed into a U-tube containing hydrochloric acid (to absorb the amine) and the gas which was also evolved was collected above mercury. 800 c.c. were obtained, the theoretical amount being about 790 c.c. This gas was evidently a chloride, for it burnt with a green flame, and on shaking with water slowly dissolved. An analysis showed that it was not pure methyl chloride, but contained probably ethyl chloride as well, for 10.2 c.c., after explosion with oxygen, gave 11.5 c.c. of carbon dioxide.

A much larger quantity of the chloride was then subjected to the action of heat. The free amines were absorbed in hydrochloric acid, and the solution of the hydrochlorides were evaporated over a water-bath nearly to dryness. The resulting liquid was then transferred to a distilling flask, and a saturated solution of caustic soda added. An oily liquid separated, which by a very gentle heat was distilled over into a fractionating flask containing solid caustic soda, and surrounded with ice. On fractionating, the dry amines were split into three portions:—

- I. Under 25° , nearly pure trimethylamine.
- II. From 25° to 45° , a mixture of trimethylamine and dimethylethylamine.
- III. From 45° to 49° , nearly pure dimethylethylamine.

These three fractions were examined in the following way:—

I. Ethyl iodide was added to the alcoholic solution of the amine and the trimethylethylammonium iodide was analysed (iodine found 59.1 per cent.; theoretical iodine = 59.0 per cent.).

II. This fraction (about 9 grams) was added to an alcoholic solution of 3 grams of ethyl iodide. By thus using a quantity of ethyl iodide only sufficient to combine with a small portion of the amine, it was thought that a separation of the two amines (dimethylethylamine and trimethylamine) might be effected, the iodide of ethyl probably uniting with the trimethylamine most readily. This was found to be the case. After the unacted on tertiary amines had been recovered and dried, on refractionating them, a further quantity was obtained boiling from 45 — 50° .

III. The third fraction was mixed with the portion boiling from 45 — 50° obtained from fraction II, and redistilled. The part which boiled from 45 — 47° was analysed and proved to be dimethylethyl amine:—

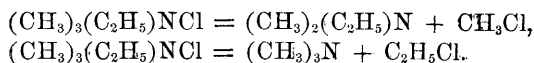
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0.2455 gram substance gave 0.5945 gram CO_2 and 0.337 gram H_2O .
 0.240 gram substance gave 40.1 c.c. of nitrogen at 14° and 752 mm.

	Calculated for $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{N}$.	Found.	
		I.	II.
C	65.75	66.04	—
H	15.07	15.25	—
N	19.17	—	19.41

This boiling point ($45\text{--}47^\circ\text{C}$.) differs from the boiling point ($39\text{--}41^\circ\text{C}$.) of the specimen of dimethylethylamine prepared from triethylamine (see p. 780). The remainder, therefore, of this third fraction was again carefully dried and distilled; eventually nearly the whole was found to boil between $42\text{--}43^\circ\text{C}$., from which we are inclined to believe that the true boiling point lies about $40\text{--}42^\circ\text{C}$.

The decomposition, therefore, of the trimethylethylammonium chloride, although yielding substantially the mixed tertiary amine, still gives at the same time trimethylamine:—



This result differs from that obtained by Lossen, who gives as the products of decomposition only dimethylethylamine and methyl chloride.

The Action of Heat on the Trimethylethylammonium Hydroxide.

This compound Lossen has shown to decompose into water, ethylene, and trimethylamine. But after the results obtained with the chloride, we thought it worth while to repeat this experiment.

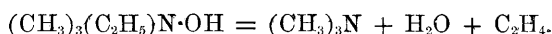
The hydroxide was prepared from the iodide by treating an aqueous solution of the salt with oxide of silver. After evaporation over a water-bath, the hydroxide was submitted to the action of heat in an ordinary distilling flask, connected with the apparatus which we invariably used during this work, namely, a U-tube filled with hydrochloric acid to absorb the free amine, and surrounded with cold water; and a gasometer to collect any gas which might be formed during the experiment. The hydroxide did not decompose till the temperature had risen above 200° ; a large quantity of gas was produced which proved to be pure ethylene. It burnt with a luminous flame and was completely absorbed by bromine, giving dibromethylene (b. p. $131\text{--}132^\circ$).

The solution of the tertiary amine in hydrochloric acid was then evaporated nearly to dryness, and the concentrated solution treated with a saturated solution of caustic soda. The free base thus

liberated was distilled over into dry alcohol, and on addition to this of ethyl iodide, a precipitate was at once obtained. This salt was converted into the platinichloride, and from the analysis was shown to be pure iodide of trimethylethylammonium:—

0·6014 gram salt gave 0·2006 gram Pt = 33·35 per cent. Pt in
 $[(\text{CH}_3)_3(\text{C}_2\text{H}_5)\text{NCl}]_2\text{PtCl}_4 = 33·38$ per cent.

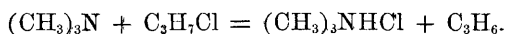
Hence the decomposition of the base may be represented by the equation:—



This result agrees with that obtained by Lossen.

Action of Heat on the Chloride and Hydroxide of Trimethylpropylammonium.

The chloride was produced by heating in a sealed tube chloride of propyl and a strong alcoholic solution of trimethylamine. The contents of the sealed tube, on evaporation over a water-bath, left a deliquescent mass, which was dissolved in water and treated with silver oxide; this solution smelt of trimethylamine, which had probably been formed by the propyl chloride being decomposed into hydrochloric acid and propylene:—



The whole of the contents of the tube were therefore treated with oxide of silver and the solution evaporated to drive off the free trimethylamine. After filtering, one half was neutralised with hydrochloric acid, and the other half was decomposed by the action of heat. A small portion of the chloride was converted into the platinichloride by adding excess of chloride of platinum and alcohol, and the precipitated salt was washed with alcohol and ether and analysed without recrystallising.

0·303 gram salt gave 0·096 gram Pt = 31·68 per cent. Pt in
 $[(\text{CH}_3)_3(\text{C}_3\text{H}_7)\text{NCl}]_2\text{PtCl}_4 = 31·86$ per cent.

The remainder of the chloride was evaporated to dryness, and heated in a flask connected with the usual apparatus for collecting the free amine and also any gas which might be formed.

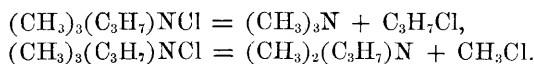
Chloride of methyl collected in the gasometer and a few drops of a liquid, presumably chloride of propyl, were noticed in the hydrochloric acid. The free tertiary amine, which was obtained from this hydrochloric acid solution, was converted by means of methyl iodide into the quaternary ammonium compound and directly analysed.

0.5525 gram took 26.936 c.c. $\frac{N}{10}$ AgNO₃ solution = 61.92 per cent.

iodine.

	Calculated for		
	(CH ₃) ₃ (C ₃ H ₇)NI.	(CH ₃) ₄ NI.	
Iodine	55.45	63.18	Found. 61.92

thus proving that the decomposition took place in probably two ways:—



The action of heat on the hydroxide yielded nearly the same results. A gas was produced which was completely absorbed by bromine, yielding a liquid which was not pure dibromethylene or dibromopropylene, its boiling point rising steadily from 130° to 140°. The hydrochlorides of the tertiary amine were converted into the quaternary ammonium compound by treatment with methyl iodide and the salt analysed.

0.5315 gram salt took 25.74 c.c. $\frac{N}{10}$ AgNO₃ = 61.51 per cent. iodine,

showing that in this case, as well as in that of the chloride, the chief product of the reaction was trimethylamine, while small quantities of dimethylpropylamine were also formed. Owing to the small quantity of the free dimethylpropylamine which we obtained, we were unable to get it in a pure state.

The Action of Heat on the Chloride and Hydroxide of Trimethylisopropylammonium.

Isopropyl iodide (prepared from glycerine) was added to a solution of trimethylamine in alcohol; after a short time, white, needle-shaped crystals of iodide of trimethylisopropylammonium iodide separated; in order to complete the reaction the solution was finally warmed. The aqueous solution of this iodide when treated with oxide of silver gave free trimethylamine, and in this respect resembled the salt obtained in the previous experiment with propyl chloride and trimethylamine; the whole was therefore treated with oxide of silver. The excess of trimethylamine was boiled off and part of the hydroxide was reserved for heating, whilst part was neutralised with hydrochloric acid to form the chloride.

An analysis of the platinichloride gave the following numbers:—

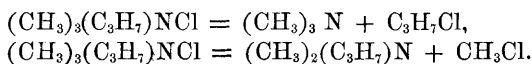
0.4555 gram salt gave 0.1460 gram Pt = 32.05 per cent. Pt in
[(CH₃)₃(C₃H₇)NCl]₂PtCl₄ = 31.86 per cent.

The chloride, on heating, decomposed yielding a gas which was not pure chloride of methyl, as about 2 per cent. was absorbed by bromine. Chloride of propyl was also formed. The free amine was treated in the usual manner with methyl iodide and then converted into the platinichloride:—

0·135 gram salt gave 0·0461 gram Pt = 34·14 per cent.

Calculated for			
Pt.....	$\overbrace{[(\text{CH}_3)_4\text{NCl}]_2\text{PtCl}_4 \quad [(\text{CH}_3)_3(\text{C}_3\text{H}_7)\text{NCl}]\text{PtCl}_4}$	Found.	
	35·07	31·86	34·14

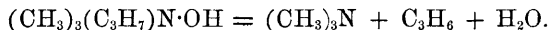
The salt therefore decomposes as follows:—



The hydroxide decomposes in a similar manner. Propylene was formed, mixed with traces of ethylene. And the tertiary amines, when converted into iodides and then into platinichlorides of the quaternary ammonium compounds, gave on analysis:—

0·4262 gram salt gave 0·1496 gram Pt = 15·10 per cent. Pt,

which showed that the decomposition was almost completely into trimethylamine, &c.:—



The Action of Heat on the Chloride and Hydroxide of Trimethylisobutylammonium.

The chloride of trimethylisobutylammonium was prepared by heating isobutyl chloride and an alcoholic solution of trimethylamine in a sealed tube. A small portion of the salt thus obtained, when treated with oxide of silver, gave a trace of free trimethylamine. Isobutyl chloride therefore resembles the haloid compounds of propyl when heated with trimethylamine, being decomposed into butylene and hydrochloric acid.

The whole of the chloride obtained from the sealed tube reaction was converted into the hydroxide and evaporated over the water-bath to purify it from the hydrochloride of trimethylamine. It was then divided into two halves; one was neutralised with hydrochloric acid, and the other was decomposed by heat.

A small quantity of the chloride was converted into the platinum double chloride and analysed:—

0·156 gram salt gave 0·0475 Pt = 30·45 gram per cent. Pt in
 $[(\text{CH}_3)_3(\text{C}_4\text{H}_9)\text{NCl}]_2\text{PtCl}_4 = 30·46$ per cent.

The remainder was evaporated to dryness and heated; it decomposed at a low temperature (below 200°) and yielded a considerable quantity of methyl chloride. The solution of tertiary amines in hydrochloric acid was treated with caustic soda and the amines distilled into alcohol. Methyl iodide was then added, and the iodides were converted into the platinichlorides. The platinum salt was fractionally crystallised.

Fraction I.—0.3019 gram Pt salt gave 0.0931 Pt = 30.83 per cent.

Fraction II.—0.2837 gram Pt salt gave 0.0871 Pt = 30.70 per cent.

Pt in $[(\text{CH}_3)_3(\text{C}_4\text{H}_9)\text{NCl}]_2\text{PtCl}_4 = 30.46$ per cent.

The decomposition is, therefore, almost wholly into the mixed amine and methyl chloride,



It may be mentioned that the chloride of trimethylisobutylammonium seems to be decomposed slightly when boiled with caustic soda solution; free dimethylisobutylamine is formed, and can be recognised by its smell.

The hydroxide seems to decompose in a manner analogous to the chloride; only traces of a permanent gas are formed, which are absorbed by bromine, while the tertiary amine was proved to be dimethylisobutylamine.

The tertiary amine was treated with methyl iodide and then converted into the platinum double chloride and analysed.

0.423 gram salt gave 0.130 gram Pt = 30.73 per cent., and the following equation represents the decomposition:—



The Action of Heat on the Chloride and Hydroxide of Trimethylisoamylammonium.

When isoamyl chloride and alcoholic solution of trimethylamine are heated together to 120° in a sealed tube, complete combination occurs, and on cooling, the tube is filled with a white, crystalline mass. A sample was converted into the double platinichloride and analysed. 0.4750 gram gave 0.1380 gram Pt = 29.0 per cent. Pt in $[(\text{CH}_3)_3(\text{C}_5\text{H}_{11})\text{NCl}]_2\text{PtCl}_4 = 29.1$ per cent. The chloride itself is a white, deliquescent solid, which, when heated to a temperature above 200°, decomposes into methyl chloride and the mixed tertiary amine,



After the free amine had been liberated from the hydrochloride

and dried over solid caustic soda, it nearly all boiled between 113° and 114°. An analysis gave the following numbers:—

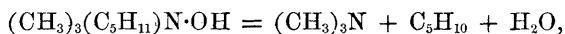
0·137 gram substance gave 0·368 gram CO₂ and 0·188 gram H₂O.
0·231 gram substance gave 24·5 c.c. nitrogen at 14° C. and 742 mm.

	Calculated for (CH ₃) ₂ (C ₅ H ₁₁)N.	Found.	
		I.	II.
C	73·04	73·25	—
H	14·78	15·27	—
N	12·17	—	12·17

As there were only traces of trimethylamine formed, the decomposition of this chloride of trimethylamylammonium seems to be almost completely into methyl chloride and the mixed tertiary amine.

The decomposition of the hydroxide is, however, different, for only a very small quantity of gas was produced when the hydroxide was heated, while an oily liquid condensed in the hydrochloric acid tube used for absorbing the tertiary amine. This liquid possessed the smell of amylene, and boiled almost at ordinary temperatures; it was treated with bromine, and the dibromide thus produced boiled with decomposition between 173° and 180°. This happens with the amylene obtained from fusel oil, the bromide boiling from 170° to 180° with partial decomposition.

The hydrochloric acid solution of the tertiary amines was evaporated, and then treated with concentrated solution of caustic soda; a large quantity of trimethylamine was liberated, which was boiled off, leaving only a very small amount of the mixed tertiary amine. The amine was extracted with ether and fractionated; only a very small quantity was obtained boiling from 110° to 115°. This was treated with methyl iodide and converted into the platinum salt. The percentage of platinum found was 29·0, while the amount required by theory is 29·1. Hence the reaction is chiefly



while a small quantity decomposes as follows:—



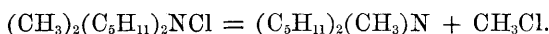
As a considerable amount of the dimethylamylamine had been obtained, an attempt was made to unite it with another molecule of amyl chloride, but even after heating for many hours at 120°, no combination occurred. The iodide of amyl was, therefore, employed, but even then the substances had to be heated in a sealed tube before combination would take place. The contents of the sealed tube was converted into the chloride, and a small portion precipitated with platinum

chloride. This salt melted below the temperature of boiling water, but could be dissolved in boiling water. On recrystallisation, it proved by analysis to be the dimethyldiamylammonium platinumchloride.

0.210 gram substance gave 0.053 gram Pt = 25.23 per cent.

Pt in $[(\text{CH}_3)_2(\text{C}_5\text{H}_{11})_2\text{NCl}]_2\text{PtCl}_4 = 25.00$ per cent.

The remainder of the chloride was heated. It was found to decompose into methyl chloride and diamylmethylamine, which latter substance, after treating with methyl iodide and being converted into the platinum salt, gave 25.38 per cent. Pt, showing that the decomposition was similar to that of the dimethylamylammonium chloride, and is represented by the following equation:—



The Action of Heat on the Chloride and Hydroxide of Trimethylallylammonium.

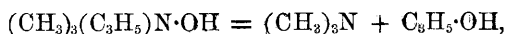
When allyl iodide is added to an alcoholic solution of trimethylamine, the reaction takes place immediately. The iodide thus formed is a deliquescent solid, which is easily soluble both in alcohol and in water.

It was converted completely into the hydroxide. The solution of the hydroxide was divided into two portions; one was neutralised with hydrochloric acid, and the other half evaporated to dryness and heated.

The decomposition of the base did not, however, yield very satisfactory results. The chief tertiary amine produced was undoubtedly trimethylamine, while the allyl radicle was decomposed, yielding considerable quantities of acrolein, which was recognised by its smell and the power it possessed of reducing a silver solution. A very small quantity of dimethylallylamine was, however, formed, for after treating with methyl iodide and converting in the usual manner into the platinumchloride, it gave the following result:—

0.1602 gram substance gave 0.514 gram Pt = 32.08 per cent.

Pt in $[(\text{CH}_3)_3(\text{C}_3\text{H}_5)\text{NCl}]_2\text{PtCl}_4 = 32.07$ per cent.; the chief reaction is therefore



and at the temperature at which the decomposition took place the allyl alcohol was decomposed, yielding acrolein amongst other products. The action of heat on the chloride yielded a similar result, only traces of the mixed tertiary amine were formed.

Both in the case of the chloride and the hydroxide, the tertiary amine produced was almost entirely trimethylamine, the allyl radicle being almost entirely destroyed during the reaction.

The Action of Heat on the Chloride and Hydroxide of Tertiary Amyl-trimethylammonium.

Trimethylamine in alcoholic solution was heated with chlorodimethylethylmethane; no combination, however, was found to occur, even after prolonged heating at 130°. The iodide was therefore substituted for the chloride. The iodide of amyltrimethylammonium which was produced was converted into the corresponding hydroxide with silver oxide, and the solution divided into two halves; one was directly subjected to the action of heat, the other was neutralised with hydrochloric acid and then decomposed also by heat.

In both cases the chief product of the decomposition was trimethylamine; only traces of the mixed amine was formed. In this respect the tertiary amyltrimethylammonium compounds differ from the isoamyl compounds obtained from trimethylamine and amyl iodide prepared from fusel oil. The trimethylamine produced by the decomposition of these compounds was identified by conversion into tetramethylammonium platinichloride.

The Action of Heat on the Chloride and Hydroxide of Trimethylphenylammonium.

The trimethylphenylammonium iodide was prepared from dimethylaniline and methyl iodide, and not directly from trimethylamine. An analysis was made of the salt. Iodine found = 48·2 per cent. Iodine in $(\text{CH}_3)_3(\text{C}_6\text{H}_5)\text{NI}$ = 48·3 per cent.

The chloride of trimethylphenylammonium is a deliquescent solid.

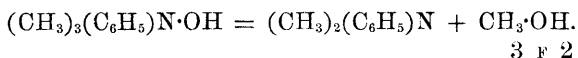
0·1920 gram substance took $9\cdot976 \frac{10}{\text{N}}$ AgNO_3 = 18·4 per cent. Cl.

Chlorine in $(\text{CH}_3)_3(\text{C}_6\text{H}_5)\text{NCl}$ = 18·5 per cent.

This salt, when subjected to the action of heat, decomposed quantitatively at a temperature much above 300° into methyl chloride and dimethylaniline, b. p. 190—192,



while the hydroxide gave exactly similar results, only the mixed tertiary amine was formed,



The Action of Heat on the Chloride and Hydroxide of Trimethylbenzylammonium.

If benzyl chloride is added to a strong alcoholic solution of trimethylamine, the reaction is extremely energetic, and when the mixture cools crystals of trimethylbenzylammonium chloride separate from the solution. A small quantity was converted into the platinum-chloride and analysed.

0.5965 gram substance gave 0.1635 gram Pt = 27.41 per cent.

Pt in $[(\text{CH}_3)_3(\text{C}_7\text{H}_7)\text{NCl}]_2\text{PtCl}_4 = 27.54$ per cent.

The chloride, when heated to a temperature slightly above 300° , decomposes, yielding both gaseous and liquid products. The gas consisted chiefly of methyl chloride, but a liquid was also formed which collected in the U-tube used for condensing the tertiary amines.

After separation from the hydrochlorides of the amines, this liquid was found to boil at $175\text{--}177^\circ$, and from its properties and boiling point was benzyl chloride.

The hydrochlorides were evaporated almost to dryness, and treated with concentrated caustic soda solution; an oily layer at once separated which, on warming, yielded a considerable amount of trimethylamine, but there also remained behind a layer of the dimethylbenzylamine. This substance was extracted with ether, dried, and distilled. After one distillation it boiled between 178° and 179° (corrected).

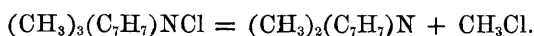
On analysis—

0.2785 gram substance gave 24.0 c.c. nitrogen at 12° C. and 759 mm.

0.2885 gram substance gave 0.8450 gram CO_2 and 0.2545 gram H_2O .

	Calculated for $(\text{CH}_3)_2(\text{C}_7\text{H}_7)\text{N}$.	Found.	
		I.	II.
C	80.00	79.88	—
H	9.63	9.80	—
N	10.36	—	10.49

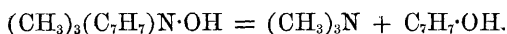
The decomposition of the chloride, when heated, is therefore largely into the mixed tertiary amines,



The action of heat on the hydroxide does not yield nearly so much of the mixed tertiary amines; benzyl alcohol being produced in con-

siderable quantities. The benzyl alcohol was identified by its boiling point and its easy conversion into benzoic acid by oxidation. The melting point of the acid was found to be $121\cdot2^\circ$, and analysis of the silver salt gave 47·53 per cent. Ag (theoretical Ag in $C_6H_5\cdot COOAg = 47\cdot16$ per cent.). There was formed also during the reaction small quantities of a solid hydrocarbon which resembled diphenyl. That some of the mixed tertiary amine was amongst the products of decomposition was proved by a small quantity of an amine, b. p. $178-180^\circ$. This was mixed with methyl iodide, and an analysis made of the platinumchloride. Platinum found = 27·7 per cent. Theoretical amount of platinum in $[(CH_3)_3(C_7H_7)NCl]_2PtCl_4 = 27\cdot5$ per cent.

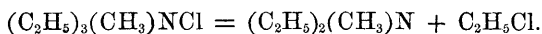
The chief mode of decomposition is therefore represented by the following equation :—



II. MIXED QUATERNARY AMMONIUM COMPOUNDS PRODUCED FROM TRIETHYLAMINE.

The Action of Heat on the Chloride and Hydroxide of Triethylmethylammonium.

These compounds were prepared in the usual way from triethylamine and methyl iodide; and the action of heat on them gave substantially the same results as those obtained by Lossen (*Annalen*, **81**, pp. 376—383). The chief portion of the chloride was found to decompose into ethyl chloride and diethylmethylamine,



The free tertiary amine was treated with methyl iodide, and after conversion into the chloroplatinate, on fractional precipitation with chloride of platinum, the following results were obtained :—

Fraction 1. 0·2368 gram salt gave 0·0753 gram Pt = 31·8 p. c.

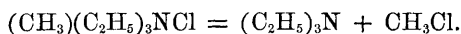
Pt in $[(CH_3)_2(C_2H_5)_2NCl]_2PtCl_4 = 31\cdot8$ „

Fraction 2. 0·251 gram salt gave 0·0778 gram Pt = 30·99 „

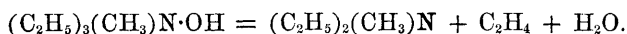
Fraction 3. 0·4172 gram salt gave 0·1303 gram Pt = 31·2 „

Pt in $[(CH_3)(C_2H_5)_3NCl]_2PtCl_4 = 30\cdot4$ „

A certain quantity of the chloride must therefore decompose into chloride of methyl and triethylamine,



The hydroxide, when heated, decomposes easily at a temperature not much above 100° , ethylene is produced, and the free tertiary amine consists *entirely* of the mixed amine,



The free base, when pure, boils at 66—67° (corrected). A combustion was made.

0·240 gram substance gave 0·604 gram CO₂ and 0·325 gram H₂O.

	Calculated for (C ₂ H ₅) ₂ (CH ₃)N.	Found.
C.....	68·96	68·64
H.....	14·94	15·05
N.....	16·09	—

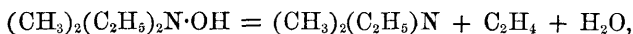
The Action of Heat on the Chloride and Hydroxide of Dimethyldiethylammonium.

A considerable amount of the diethylmethylamine was treated with methyl iodide. The two substances united with the evolution of heat. Some of the iodide was analysed.

0·622 gram salt required 27·01 c.c. $\frac{N}{10}$ AgNO₃ solution = 55·4 p. c. I.

Iodine in (C₂H₅)₂(CH₃)₂NI = 55·4 ,,

As Lossen had already heated the chloride and found a mixture of tertiary amines resulted, we did not repeat his experiment. The decomposition, however, of the hydroxide, although believed by him to take place as follows:—



had not been tried. This result was conjectured by Lossen from the results of Hofmann, who found that usually in a mixed quaternary ammonium hydroxide, the ethyl-group was first eliminated (as ethylene) when the compound was decomposed by heat. This conjecture of Lossen proved to be correct, for on heating the dimethyldiethylammonium hydroxide we obtained a tertiary amine which, when treated with methyl iodide, and converted into the platinum salt, gave the following numbers:—

0·302 gram salt gave 0·100 gram Pt..... = 33·1 per cent.

Pt in [(CH₃)₃(C₂H₅)NCl]₂PtCl₄ = 33·3 ,,

The ethylene was identified by absorbing it with bromine and taking the boiling point of the dibromethylene (b. p. 131·2°).

A curious point, however, was noticed with regard to the boiling point of the dimethylethylamine—it boiled completely between 39° and 41°. Now, the dimethylethylamine obtained by the action of heat on trimethylethylammonium chloride boiled from 42° to 43° (p. 770). We have repeated the former experiment again with

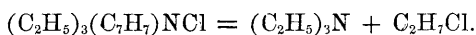
much larger quantities of salt, and with identically the same result; *the whole of the dimethylethylamine boils between 39—41°*. It has recently been suggested by Hantsch and Werner (*Ber.*, **23**, 11—30) that two isomers of the form $\text{NR}'\text{R}''$ are possible; whether we have here such substances we are unable to say at present, but propose to continue the investigation.

The Action of Heat on the Chloride and Hydroxide of Triethylbenzylammonium.

Triethylamine reacts at once with benzyl chloride when the two are mixed together. The chloride thus produced can be obtained in the crystalline form from a concentrated aqueous solution, but attempts to determine the water of crystallisation in it were unsuccessful, the salt decomposing when heated above 100°. The chloride was decomposed in the usual manner. Benzyl chloride was formed in considerable quantities and recognised by its smell and boiling point (178—7°). The free tertiary amines consisted almost entirely of triethylamine, only a very small quantity of the mixed amine being formed. The triethylamine was converted into tetrethylammonium iodide, and an iodine estimation made. Iodine found = 49·38 per cent. Iodine in $(\text{C}_2\text{H}_5)_4\text{NI}$ = 49·41 per cent. The less volatile base was mixed with ethyl iodide and converted into the platinum-chloride.

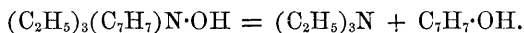
0·435 gram gave 0·1082 gram Pt = 24·87 per cent.
Pt in $[(\text{C}_2\text{H}_5)_3(\text{C}_7\text{H}_7)\text{NCl}]_2\text{PtCl}_4$ = 24·62 ,,

The chief decomposition which the chloride therefore undergoes when heated is—



This agrees with the decomposition of the iodide, for Bodewig has found (*Jahresbericht*, 1879, 435) that triethylbenzyl ammonium iodide when heated yields benzyl iodide and triethylamine. The hydroxide when heated seems to yield similar results; only traces of the mixed tertiary amine are produced. The benzyl alcohol was converted into benzoic acid and an analysis of the silver salt made (47·23 per cent. Ag found. Ag in $\text{C}_6\text{H}_5\text{COOAg}$ = 47·16 per cent.).

The decomposition of the base is chiefly as follows :—

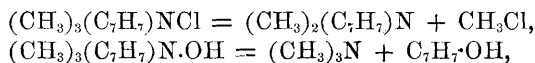


An interesting point with regard to these triethylbenzylammonium compounds has been raised by Ladenburg (*Ber.*, **10**, 45); he holds that the iodide prepared by the action of diethylbenzylamine on ethyl

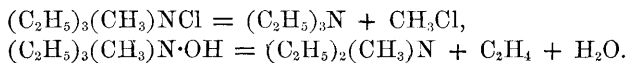
iodide is not identical with that produced from the chloride obtained when triethylamine is allowed to react with benzyl chloride. We are at present engaged in preparing a number of these mixed quaternary ammonium compounds, and propose to study the properties of their salts, particularly the platinichlorides.

Conclusion.

From the forgoing results, it evidently seems to be a general rule that when a mixed quaternary ammonium chloride or hydroxide (made from trimethylamine or triethylamine) is heated, *a mixed tertiary amine is always produced*. The actual amount formed, however, varies very considerably with different compounds; for with the trimethylphenylammonium chloride the only product is dimethylphenylamine, whilst with the allyl- and isopropyl-trimethylammonium compounds, the chief tertiary amine formed by the action of heat is trimethylamine. If we take the chlorides, the *methyl-group* seems to be very easily eliminated from the molecule as *methyl chloride*, whilst in the case of the hydroxides the *ethyl-group* almost invariably splits away as ethylene. The reaction, therefore, seems to be more influenced by the nature of the decomposition products than by the introduced radicles; and we sometimes find that the chloride gives a much larger quantity of the mixed tertiary amine than the hydroxide:—



whilst in other cases we find the reverse to be the case:—



Owing to the limited quantities of trimethylamine and triethylamine which we had to work with, the properties and boiling points of some of the mixed tertiary amines could not be determined; but as we propose to continue the research in somewhat the same direction with the view of studying the asymmetry of the nitrogen-atom, we may be able to fill up some of these gaps in a communication which we hope to bring before the Society at a future date.

*University College,
London.*