# CXXXIX.—*The Nature of the Alternating Effect in Carbon Chains. Part XVIII. Mechanism of Exhaustive Methylation and its Relation to Anomalous Hydrolysis.*

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THE decomposition of quaternary ammonium compounds has been extensively investigated and often exploited for the synthesis of olefins and the degradation of complex bases; nevertheless, no general theory of the mechanism of the process seems to have been advanced. Unquestionably the facts to be explained are numerous and complex; in particular, a satisfactory theory should embrace the following points :

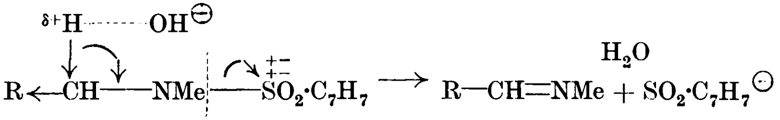
(1) The hydrogen atom eliminated along with hydroxyl in the reaction $R\cdot CH_2\cdot CH_2\cdot NR'_3\cdot OH = R\cdot CH{:}CH_2 + NR'_3 + H_2O$ is apparently one of those attached to the second carbon atom from the nitrogen atom. Assuming that this is definitely the case (below), then, since one can hardly suppose otherwise than that the cause of molecular instability originates in the ammonium group, it must be explained, first, how the necessary reactivity is propagated to such a distant hydrogen atom through two intervening *saturated* carbon atoms without imparting *en route* a still greater reactivity to the hydrogen atoms attached to the first carbon atom, and, secondly, why the transmitted effect emerges just where it does.

(2) When the four alkyl groups attached to the nitrogen atom are such that different olefins might be produced by decomposition in different directions, the one actually formed has always been found to be ethylene if an ethyl group is present. It is shown below that this generalisation, sometimes referred to as Hofmann's rule, is subject to certain exceptions : the reasons for the rule and the causes of the exceptions both require elucidation.

(3) The synthesis of olefins from quaternary ammonium hydroxides sometimes fails owing to the elimination of an alcohol : $R^1R^2R^3R^4N\cdot OH = R^1R^2R^3N + R^4\cdot OH$. It is desirable to be able to foretell when and to what extent this is likely to take place.

(4) Quaternary ammonium salts (*e.g.*, chlorides) often decompose differently from the hydroxides. In certain cases both chlorides and hydroxides give corresponding products, but where a difference exists it is the hydroxide which yields the olefin and the salt which gives the alkyl halide or ester. Moreover, the chloride usually decomposes less easily than the corresponding hydroxide. Since both are strong electrolytes and the organic ion is the same in each, these differences of reactivity and their lack of complete uniformity both require explanation.

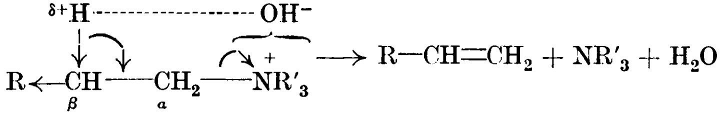
The hypothesis which, we believe, suffices to interpret all these phenomena was outlined in Part IV (J., 1926, 1305) in connexion with hydrolysis, and may be expressed in general terms as follows : Hydrogen atoms in organic molecules, even those in hydrocarbon radicals, exist to a greater or less degree in a condition of incipient ionisation depending on the electron-affinity of the surrounding groups, $\leftarrow C \leftarrow H(\delta +)$; when a hydrogen atom is abstracted as hydrion by a reagent having sufficient proton-affinity to effect its removal in this form, the electrons which held it become absorbed into the residue of the molecule in a manner which again is determined by the electron-affinity of the groups present. The proton-affinity of a reagent is measured by the electrolytic dissociation of its compound with a hydrogen ion; thus the hydroxide ion must have a large proton-affinity, since water is scarcely dissociated. The electron-affinities of groups may be inferred from their influence on the strengths of acids and bases (Lewis), their effect on the mobility of tautomeric systems (Ingold, Shoppee, and Thorpe, J., 1926, 1427), their orienting action in additions (Lucas and Moyse, *J. Amer. Chem. Soc.*, 1925, **47**, 1459) and substitutions (compare *Ann. Reports*, 1926, 129), and their effect on the dipole moments of molecules (compare *loc. cit.*). The hypothesis was tested in Part IV through the theoretical deduction that sulphonamides on *alkaline* hydrolysis ought to yield, not the normal sulphonic acid and amine, but a sulphinic acid (*i.e.*, sulphinate ion) and an imine, provided that the electron-affinity of R is sufficient.



$$\begin{array}{l} {}^{\delta+}\mathrm{H}\cdots\cdots\mathrm{OH}^{\ominus} \\ \mathrm{R{\leftarrow}CH{-}NMe{-}\overset{+-}{S}O_2{\cdot}C_7H_7} \longrightarrow \mathrm{R{-}CH{=}NMe} + \overset{\mathrm{H_2O}}{\mathrm{SO_2{\cdot}C_7H_7}^{\ominus}} \end{array}$$

A consideration of the strengths as acids or bases of such compounds as phenol and aniline suggests that the phenyl group can exert a moderate electron-attraction, and in the case $R = C_6H_5$ the above anomalous mode of hydrolysis was realised. The direction of the disruption in this and all similar cases is determined by the circumstance that, as the hydroxide ion draws off the proton, so the electrons relieved from its attraction move towards the positively charged (sulphur) atom.

The application to the decomposition of quaternary ammonium hydroxides is obvious: the positive pole to which the liberated electrons move is the ammonium nitrogen atom, and it is unnecessary to add an alkali because the compound contains its own hydroxide ions:



$$\begin{array}{l} {}^{\delta+}\mathrm{H}\cdots\cdots\cdots\cdots\mathrm{OH}^{-} \\ \mathrm{R{\leftarrow}\underset{\beta}{CH}{-}\underset{\alpha}{CH_2}{-}\overset{+}{N}R'_3} \longrightarrow \mathrm{R{-}CH{=}CH_2} + \mathrm{NR'_3} + \mathrm{H_2O} \end{array}$$

We may now consider how this hypothesis applies to the four points mentioned at the outset.*

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* It is not attempted to distinguish between the possible variations of the general mechanism, *e.g.*, possible lack of complete synchronisation of the electron transfers. The intention is to present only a preliminary survey of the field; each of the aspects thus outlined will be made the subject of a future, more detailed communication.

(1) The only alternative to the view that a β-hydrogen atom enters into the constitution of the eliminated water molecule is that one of the α-hydrogen atoms is first removed, the bivalent-carbon compound (sextet) so formed undergoing rearrangement :

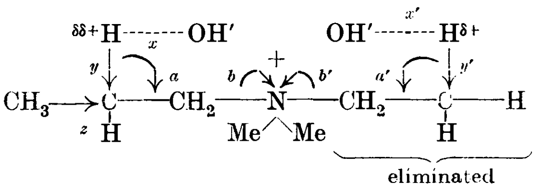
$$\{CH_3{\cdot}CH_2{\cdot}NR_3\}^{\cdot}\,OH' \longrightarrow CH_3{\cdot}CH\colon \longrightarrow CH_2\colon CH_2$$

There are many arguments against this theory; *e.g.*, ethylene has never been detected amongst the decomposition products of tetramethylammonium hydroxide, nor has stilbene been obtained from benzyltrimethylammonium hydroxide; yet these products would be expected to appear if a bivalent carbon compound intervened. Positive evidence against the rearrangement theory is provided by the observation that alkyltrimethylammonium hydroxides, which have no α-hydrogen atoms, decompose in the normal manner (Kohn, Schlegl, and Morgenstern, *Monatsh.*, 1907, **28**, 491, 525; compare p. 1004) :

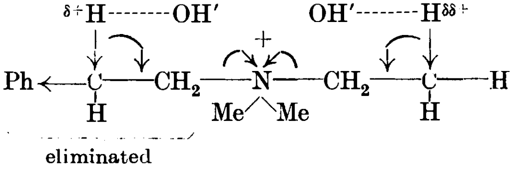
$$\{R{\cdot}CH_2{\cdot}CMe_2{\cdot}NMe_3\}^{\cdot}\,OH' \longrightarrow R{\cdot}CH\colon CMe_2 + NMe_3 + H_2O$$

Therefore it seems certain that it is one of the β-hydrogen atoms which is originally eliminated; and the mechanism suggested necessitates the direct abstraction of this hydrogen atom, since the removal of no other would enable the mutually accommodating *integral* electron displacements to occur with preservation of the octets.

(2) The rule that ethylene is eliminated in preference to any higher unsaturated hydrocarbon in quaternary ammonium hydroxide distillations is one to which we cannot call to mind any recorded exception. It is true that, as in Hofmann's original instances, *e.g.*, amyltriethylammonium hydroxide, most of the examples by which the rule has been illustrated are affected by the circumstance that several ethyl groups were present in the ammonium compound, which might therefore be predisposed to eliminate ethylene owing to statistical factors. This is not so, however, in the case of *dimethylethyl*-n-*propylammonium hydroxide*, which, as we have found, also yields mainly ethylene, and only a very little propylene. This is in agreement with the foregoing hypothesis; for, since alkyl groups repel their shared electrons more than does hydrogen (Lucas), the terminal methyl group of the propyl chain will reduce ($z$) the incipient ionisation ($y$) of the propyl β-hydrogen atom below that ($y'$) of the ethyl β-hydrogen atom. That is to say, the extraction of the propyl proton by a hydroxide ion ($x$, $y$), and the dependent decomposition ($a$, $b$), will be hindered relatively to the extraction of the ethyl proton ($x'$, $y'$) and its dependent decomposition ($a'$, $b'$) :



Similarly, it follows that dimethyl-*n*-propyl-*n*-butylammonium hydroxide should yield more propylene than butylene, that dimethyl-*n*-butyl-*iso*butylammonium hydroxide should give *n*-butylene, and not *iso*butylene, as the main olefinic product; many similar predictions may be made; it is also clear that the only reason why no exception has previously been found to the Hofmann rule is that the groups with which ethyl has been placed in competition have hitherto all been of one type, namely, $-CH_2{\cdot}CH_2R$ or $-CH_2{\cdot}CHR_2$, where R has a smaller electron-affinity than hydrogen. Hence, if R were phenyl, the rule should be disobeyed—a deduction we have tested and found correct:



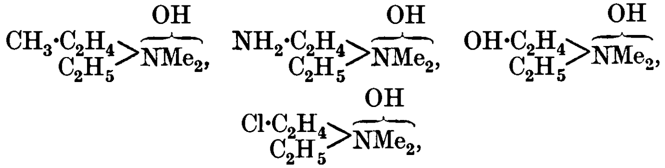
Again, a β-*p*-nitrophenylethyl group should be more readily eliminated as olefin than an unsubstituted β-phenylethyl group, and this also we have verified.

Thus it is possible to construct a series representing the relative ease of elimination of groups as olefins, and the sequence established by the above experiments,

$$CH_3{\cdot}CH_2{\cdot}CH_2 < H{\cdot}CH_2{\cdot}CH_2 < C_6H_5{\cdot}CH_2{\cdot}CH_2 < NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2,$$

could, of course, be filled in with many other groups from theoretical considerations. It should also be emphasised that such a series indicates not only the direction of a particular decomposition, but also the ease with which it will take place. Thus we found that decompositions resulting in the elimination of propylene or ethylene always required a fairly high temperature, whereas that which gave styrene occurred in hot dilute aqueous solution, and that which yielded *p*-nitrostyrene took place during the attempted preparation of the quaternary compound, which we were unable to isolate for this reason.

One more example may be given. From the probable increasing electron-affinity of the groups in the series $CH_3$, $NH_2$, OH, Cl—as indicated, for example, by the increasing proportion of *m*-substitution in $CH_3\cdot COPh$, $NH_2\cdot COPh$, $OH\cdot COPh$, $Cl\cdot COPh$ (Cooper and Ingold, this vol., p. 836)—it follows that the ammonium hydroxides



$$\genfrac{}{}{0pt}{}{CH_3\cdot C_2H_4}{C_2H_5}>\overbrace{NMe_2}^{OH},\quad \genfrac{}{}{0pt}{}{NH_2\cdot C_2H_4}{C_2H_5}>\overbrace{NMe_2}^{OH},\quad \genfrac{}{}{0pt}{}{OH\cdot C_2H_4}{C_2H_5}>\overbrace{NMe_2}^{OH},$$

$$\genfrac{}{}{0pt}{}{Cl\cdot C_2H_4}{C_2H_5}>\overbrace{NMe_2}^{OH},$$

should yield successively diminishing proportions of ethylene and increasing proportions of dimethylethylamine on decomposition. This appears to be the case. The main products obtained from the first compound are ethylene and dimethylpropylamine; the second gives corresponding principal products ethylene and β-aminoethyldimethylamine, but in addition yields acetaldehyde (evidently derived from vinylamine) and an appreciable quantity of dimethylethylamine; the third compound of the series yields still less ethylene, and appears to give more acetaldehyde (vinyl alcohol), and nearly equal amounts of dimethylethylamine and β-hydroxyethyldimethylamine; finally, the chloro-compound yields no appreciable quantity of ethylene, but gives a basic product consisting mainly of dimethylethylamine—another exception to Hofmann's rule.

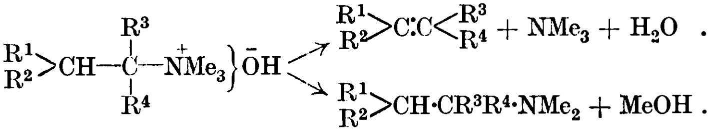
It will be evident from these examples that the decomposition of quaternary ammonium hydroxides furnishes a means of comparing electron-affinities which should be capable of many applications.

(3) In the above examples, the ammonium atom achieves neutrality by the appropriation of electrons which become available as a direct consequence of the withdrawal of a β-hydrion from one of the alkyl groups. It may happen, however, (i) that this mechanism cannot function owing to the absence of β-hydrogen atoms, (ii) that it either cannot function, or can do so only with great difficulty, owing to the more or less effective stabilisation of all the existing β-protons by the strong electron-repulsion of neighbouring groups. In these cases, the only other means open to the nitrogen atom is to extract the shared electrons from a group without the independent facilitation of a compensating supply of electrons for the depleted carbon atom; in this event, the group is ejected as a positive ion, which will at once unite with any negative ion that happens to be present in the liquid, so that in the decompositions now under consideration it appears as an alcohol (compare following section):

$$R'R''R'''\overset{+}{N}\overset{\curvearrowleft}{\text{——}}R+\overset{-}{O}H=R'R''R'''N+\overset{+}{R}+\overset{-}{O}H=$$
$$R'R''R'''N+R\cdot OH.$$

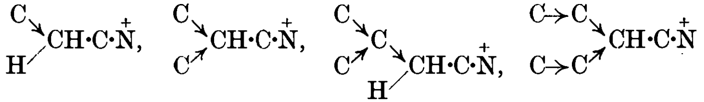
Which of the four groups will thus be eliminated, and the facility of the process, will depend on the relative stabilities of the possible positive ions, and these in turn can be inferred, for example, from the reactivities of the iodides RI, R'I, R''I, R'''I towards the same ionising substance. Thus, amongst the commoner groups devoid of an available β-hydrogen atom the order of ease of elimination should be $Ph_3C > Ph_2CH > PhCH_2 > CH_3 > Ph$, and this has been confirmed for the last three groups by Collie and Schryver (J., 1890, **57**, 767), who found that benzyltrimethylammonium hydroxide yielded benzyl alcohol, whilst phenyltrimethylammonium hydroxide gave methyl alcohol on distillation.

In considering the relative ease of elimination of any *one* group as alcohol from various ammonium hydroxides which can also yield an olefin, we may take for illustration the elimination of methyl alcohol, since this is the case which usually arises in exhaustive methylations. If the quaternary hydroxide is of the form $\{AlkNMe_3\}^{\cdot}OH'$, the possible decompositions are:



$$\begin{matrix} & \nearrow & {}^{R^1}_{R^2}{>}C{:}C{<}^{R^3}_{R^4} + NMe_3 + H_2O \quad . \quad (A) \\ \left.{}^{R^1}_{R^2}{>}CH{-}\overset{R^3}{\underset{R^4}{C}}{-}\overset{+}{N}Me_3\right\}\overset{-}{O}H & & \\ & \searrow & {}^{R^1}_{R^2}{>}CH{\cdot}CR^3R^4{\cdot}NMe_2 + MeOH \quad . \quad (B) \end{matrix}$$

Now since (B) takes place only when (A) is inhibited, it follows that the occurrence of (B) depends primarily on the electron-repulsion of $R^1$ and $R^2$; it will depend only to a small extent on the groups $R^3$ and $R^4$, because any electronic strain set up by these radicals can reach the β-hydrogen atom only indirectly. From a consideration of strain-paths such as



it can be seen that the order of the effects due to alkyl groups $R^1$ and $R^2$ should be: $CH_3{\cdot}[CH_2]_n > CH_3{\cdot}[CH_2]_{n-1} > \ldots\ldots > CH_3 > H$; and $(CH_3)_2 > CH_3{\cdot}CH_2$, $(CH_3)_2CH > CH_3{\cdot}[CH_2]_2$, etc.; or, in words, longer chains should be more effective than shorter, and branched chains more effective than isomeric normal chains. Also it would be expected that the effect of the more remote parts of long chains would be small in comparison with that of the portions nearer the β-hydrogen atom.

The following table shows how far these conclusions are supported by experimental data relating to the effect of alkyl groups on the elimination of methyl alcohol from hydroxides of the type $\{AlkNMe_3\}^{\cdot}OH'$.

*Decomposition of Trimethylalkylammonium Hydroxides.*

| No. | Alkyl group. | $R^1$. | $R^2$. | $R^3$. | $R^4$. | Reaction B (%). |
|---|---|---|---|---|---|---|
| 1 | Ethyl. | H | H | H | H | 0 |
| 2 | *iso*Propyl. | H | H | $CH_3$ | H | 0 |
| 3 | *sec.*-Butyl. | H | H | $CH_3{\cdot}CH_2$ | H | Small. |
| 4 | *sec.*-Amyl. | H | H | $CH_3{\cdot}CH_2{\cdot}CH_2$ | H | Small. |
| 5 | *tert.*-Butyl. | H | H | $CH_3$ | $CH_3$ | Small. |
| 6 | *n*-Propyl. | $CH_3$ | H | H | H | 19 |
| 7 | *n*-Butyl. | $CH_3{\cdot}CH_2$ | H | H | H | 25 |
| 8 | *iso*Butyl | $CH_3$ | $CH_3$ | H | H | 37 |
| 9 | β-Ethyl-*n*-butyl. | $CH_3{\cdot}CH_2$ | $CH_3{\cdot}CH_2$ | H | H | 57 |
| 10 | β-*n*-Propyl-*n*-amyl. | $CH_3{\cdot}CH_2{\cdot}CH_2$ | $CH_3{\cdot}CH_2{\cdot}CH_2$ | H | H | 69 |

The figures for examples (1) and (2) are taken from Collie and Schryver's published results; the experimental basis for the remainder is recorded in this paper, but example (6) was investigated also by Collie and Schryver, whose observations accord with the figure given. In addition to these results, data have been recorded by von Braun (*Annalen*, 1911, **382**, 1) which appear to establish the anticipated sequence of alkyl groups :

*n*-Butyl$<$*n*-Amyl$<$*n*-Hexyl$<$*n*-Heptyl, *n*-Octyl, . . . . . . *n*-Cetyl

but these are not included in the table, because, although they are in the correct order relatively, we doubt their essential accuracy : certainly, von Braun's results for trimethyl-*n*-butylammonium hydroxide differ widely from ours, and it is proposed to reinvestigate the other cases. In the meantime it is quite clear (i) that β-alkyl substituents ($R^1$, $R^2$) are more effective than α-alkyl groups ($R^3$, $R^4$) in promoting reaction B, (ii) that the rule for normal chains holds at least for the lower members : $H<CH_3<C_2H_5<C_3H_7$, and (iii) that a comparison of the *n*- and *iso*butyl-compounds exemplifies the predicted effect due to the branching of carbon chains.

(4) It follows from the basic hypothesis that the ease of removal of the β-proton (reaction A) depends (*a*) on its vulnerability, (*b*) on the proton-avidity of the attacking anion. Factor (*a*) has been discussed (Section 3); now it is necessary to consider factor (*b*).

In order to maintain factor (*a*) constant, we must consider a *single* ammonium ion, and the example chosen for experimental study was No. 6 in the table. Now a precise measure of the proton-affinity of an attacking anion X′ would be available if the electrolytic dissociation constant of the compound $HX(\rightleftharpoons H^{\cdot} + X')$ under the conditions of the decomposition (*i.e.*, in the fused material) were known. Such data, however, are not available, and in their absence the most acceptable criterion is the dissociation constant in water or some other solvent. Adopting this view, and remembering that it may possibly lead to anomalies, since the relative strengths of electrolytes are known to be sometimes inverted on passing from non-aqueous solvents to water, it follows that reaction (A′) might be successively inhibited and (B′) correspondingly favoured on passing through such a series as the quaternary hydroxide, phenoxide, nitrophenoxide, chloride; thus, since the hydroxide gives 19% of methyl alcohol, the phenoxide should yield a greater proportion of anisole, and a nitrophenoxide still more nitroanisole, for phenol is a stronger acid than water, and the nitrophenols are stronger than phenol.

$$C_3H_7\cdot\overset{+}{N}Me_3\Big\}\;\overset{-}{X}\begin{array}{ll}\nearrow C_3H_6 + NMe_3 + HX \quad . \quad . \quad . & (A')\\ \searrow C_3H_7\cdot NMe_2 + MeX \quad . \quad . \quad . & (B')\end{array}$$

Actually our yields of anisole and *m*-nitroanisole were 65% and 89% respectively, and experiment establishes the following relationships amongst trimethyl-*n*-propylammonium hydroxide and six of its salts.

$$\begin{array}{c}\text{——— Increasing “B′” ———}\rightarrow \qquad \leftarrow\text{———}\\ \text{Hydroxide} < \left\{\begin{array}{l}\text{Phenoxide}\\ \text{Carbonate}\end{array}\right. < \left\{\begin{array}{c}m\text{-Nitrophenoxide}\\ \text{Acetate}\end{array}\right. > \left\{\begin{array}{l}\text{Chloride}\\ \text{Iodide}\end{array}\right.\\ \leftarrow\text{——— Decreasing “A′” ———} \qquad \text{———}\rightarrow\end{array}$$

The first five substances are thus related in accordance with the tentative prediction based on aqueous acid-strengths, but the halogen salts are anomalous, since they give slightly more olefin than the nitrophenoxide or acetate. There is, however, nothing demonstrably inconsistent with the general theory in this behaviour, because the halogen acids are known to be almost wholly undissociated in most non-aqueous solvents, and it is not impossible that under the conditions of the decompositions hydrogen chloride and hydrogen iodide may be weaker acids than acetic acid.* The other conceivable source of disturbance, namely, the effect of the anions in directly facilitating the removal of the positive alkyl ions, we do not regard as likely to produce large irregularities, since, owing to the protection of the positive carbon nucleus by its surrounding shell of electrons, the direct attraction between that nucleus and any circumambient anions would presumably be relatively feeble.

## EXPERIMENTAL.

(I). *Dimethylethyl-*n*-propylammonium Hydroxide.*—A modification of Eschweiler's method (*Ber.*, 1905, **38**, 881) was used for the preparation of dimethylethylamine. The solution obtained by neutralising 13·5 c.c. of 33% aqueous ethylamine with hydrochloric acid

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* Hydrogen chloride is a non-conductor of electricity, but solutions of acetic acid in hydrogen chloride are good conductors (Archibald, *J. Amer. Chem. Soc.*, 1907, **29**, 1471).

was evaporated to a paste, which was then heated with 38% formaldehyde (20 c.c.) under pressure at 140—150° for 3—4 hours. The product of several such experiments was evaporated to a paste, which was treated with solid potassium hydroxide, the evolved bases, b. p. 30—40° (the greater part had b. p. 36°), being collected in well-cooled ether. The dimethylethylamine thus obtained was not pure, since it gave a non-crystalline quaternary iodide with *n*-propyl iodide. The tertiary base was therefore converted into its picrate with benzene–ethereal picric acid, and the salt crystallised from alcohol until its m. p. rose to and remained constant at 200—201°. The pure picrate was converted into the hydrochloride by shaking a suspension in hydrochloric acid with benzene; the free base, b. p. 36—38°, was then liberated.

The following method also was used. Well-dried ethylamine hydrochloride, prepared from 120 g. of 33% aqueous ethylamine, was thoroughly mixed with 90 g. of paraformaldehyde and heated under reflux for 2·5 hours at 135° (internal temperature). The product was covered with ether and decomposed with concentrated aqueous sodium hydroxide, and the ethereal solution of the base (it is undesirable to extract more than once with ether) was precipitated with ethereal picric acid (150 g.). The picrate was collected from the still warm suspension (the salt which subsequently separates being very impure), crystallised twice from water to remove a sparingly soluble oily product, converted into the hydrochloride and thence into the free base (yield, 25 g.).

A mixture of this (19 g.) with *n*-propyl iodide (50 g.) was kept for 4 days at the ordinary temperature, and the hygroscopic *dimethylethyl*-n-*propylammonium iodide* thus obtained was converted into the *picrate* by treatment with saturated aqueous sodium picrate. This salt separates from alcohol or water in orange-yellow needles or tablets, m. p. 185—187° (Found : C, 45·55; H, 6·0. $C_{13}H_{20}O_7N_4$ requires C, 45·35; H, 5·8%).

*Decomposition of dimethylethyl*-n-*propylammonium hydroxide.* A solution of this substance prepared from the iodide, silver oxide, and water was distilled through four wash-flasks. The first two contained 3*N*-hydrochloric acid, and the second two bromine, the first, third, and fourth being cooled in ice-water. Usually the decomposition products were completely trapped in the first and the third vessel.

Methyl alcohol was detected by distilling the hydrochloric acid solution and treating the first portion of the distillate with *p*-nitrobenzoyl chloride and alkali; a small amount of methyl *p*-nitrobenzoate, m. p. 92°, was then formed.

The olefin bromide, obtained after destruction of the excess of bromine with freshly prepared sodium hydrogen sulphite, boiled completely at 131—132° (ethylene dibromide has b. p. 131°, propylene dibromide has b. p. 140°) and therefore consisted mainly of ethylene dibromide (Found: C, 13·2; H, 2·3%). The material was fractionally distilled, and analysis of the last few drops, b. p. about 132° (Found: C, 15·5, 15·2; H, 2·3, 2·35; Br, 82·1, 82·3. Calc. for $C_2H_4Br_2$: C, 12·8; H, 2·1; Br, 85·1. Calc. for $C_3H_6Br_2$: C, 17·8; H, 3·0; Br, 79·2%) showed that some propylene dibromide was present.

Confirmatory results were obtained on examining the basic decomposition products, which were first converted into their picrates. Analysis of the crude mixture indicated *dimethyl-*n-*propylammonium picrate* to be the principal constituent (Found: C, 41·9, 41·7; H, 4·9, 5·1. $C_{11}H_{16}O_7N_4$ requires C, 41·8; H, 5·1%), and 70% of this substance was readily isolated in stout, lemon-yellow prisms, m. p. 108—109°, by crystallisation from ethyl acetate (Found: C, 41·9; H, 5·4%). It was identified by conversion into trimethyl-*n*-propylammonium picrate, m. p. 195° (below). The residue was repeatedly fractionally crystallised from toluene and ethyl acetate, used for the most part alternately; besides a further quantity of dimethyl-*n*-propylammonium picrate, a small amount of dimethylethylammonium picrate (identified by mixed m. p.) was thus obtained, together with a residue which may have contained methylethylpropylammonium picrate, although we did not succeed in isolating this.

The hydroxide therefore decomposes mainly into dimethylpropylamine and ethylene, to a small extent into dimethylethylamine and propylene, and also to a slight extent into methyl alcohol and, presumably, methylethylpropylamine. This seems to be the first recorded instance of the formation of methyl alcohol in the decomposition of a quaternary ammonium hydroxide which also yields ethylene.

(II). β-*Phenylethyldimethylethylammonium Hydroxide.*—β-Phenylethyldimethylamine (Goss, Hanhart, and Ingold, this vol., p. 250) liberated from 28 g. of the picrate was warmed with a benzene solution of ethyl iodide (20 g.) for 2 hours on the water-bath. The *iodide* was collected (22 g.) and crystallised twice from alcohol–ethyl acetate; m. p. 158—159°. It is easily soluble in water, alcohol, and chloroform (Found: C, 47·5; H, 6·9. $C_{12}H_{20}NI$ requires C, 47·2; H, 6·6%).

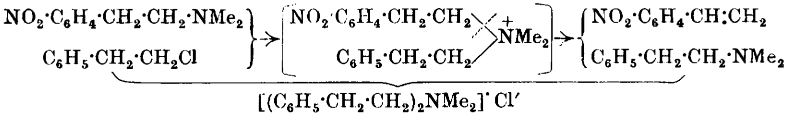
The *picrate* appears to form two crystallographic modifications. The precipitate obtained by adding sodium picrate solution to an aqueous solution of the iodide melts at about 113°, and on crystallisation from alcohol forms well-defined, lemon-yellow needles, m. p.

96—97°. If, however, the needles are mixed with a trace of the crude product the m. p. is 115—116°, and if the melt obtained by heating the needles to just above 97° is treated with a " speck " of the crude powder, solidification at once occurs and the product then melts at 115—116°. The needles are only slightly soluble in cold ethyl alcohol, but are readily soluble in acetone (Found : C, 53·5; H, 5·6. $C_{18}H_{22}O_7N_4$ requires C, 53·2; H, 5·4%).

*Decomposition of* β-*phenylethyldimethylethylammonium hydroxide.* The aqueous solution of the hydroxide, prepared from the iodide and an aqueous suspension of silver oxide, began to decompose at 100°. The products were exclusively styrene and dimethylethylamine, both of which were isolated in the pure condition in excellent yield. The former, b. p. 140—143°, was characterised through its dibromide, m. p. 74°, which was compared with an authentic specimen. The latter was converted into its picrate, which formed large, lustrous, yellow leaves, m. p. 202—203° (not needle-like crystals, m. p. 193—194°, as described by Kohn and Morgenstern, *Monatsh.*, 1907, **28**, 496), and was identified by direct comparison and by analysis (Found : C, 40·0; H, 4·6. Calc. : C, 39·7; H, 4·6%).

In order to detect any decomposition in the direction leading to ethylene and β-phenylethyldimethylamine, a portion of the basic product was oxidised with permanganate under conditions in which this base yields benzoic acid quantitatively (Goss, Hanhart, and Ingold, *loc. cit.*). Benzoic acid was not obtained, and an experiment designed to detect the evolution of small amounts of ethylene also yielded a negative result.

(III). *Attempted Preparation of* p-*Nitrodi*(β-*phenylethyl*)*dimethylammonium Chloride from* β-*Phenylethyl Chloride and* p-*Nitro*-β-*phenylethyldimethylamine ; Formation of* p-*Nitrostyrene,* β-*Phenylethyldimethylamine and Di*(β-*phenylethyl*)*dimethylammonium Chloride.*—We regard these experiments as showing that the *p*-nitrodi(β-phenylethyl)dimethylammonium ion is unstable under the experimental conditions owing to the great tendency to the elimination of the *p*-nitrophenylethyl group as nitrostyrene. The only quaternary salt which could be isolated from the product of interaction of β-phenylethyl chloride and *p*-nitro-β-phenylethyldimethylamine was di(β-phenylethyl)dimethylammonium chloride, the formation of which we explain as follows :



$$\underbrace{\left.\begin{matrix} NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_2 \\ C_6H_5\cdot CH_2\cdot CH_2Cl \end{matrix}\right\} \rightarrow \left[\begin{matrix} NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2 \\ C_6H_5\cdot CH_2\cdot CH_2 \end{matrix} \overset{+}{>} NMe_2\right] \rightarrow \left\{\begin{matrix} NO_2\cdot C_6H_4\cdot CH{:}CH_2 \\ C_6H_5\cdot CH_2\cdot CH_2\cdot NMe_2 \end{matrix}\right.}_{[(C_6H_5\cdot CH_2\cdot CH_2)_2NMe_2]^{\cdot}\,Cl'}$$

Experiments were carried out under various conditions, but with substantially identical results; the following is typical.

*p*-Nitro-β-phenylethyldimethylamine, liberated from 20 g. of the pure oxalate, was heated with a slight excess of β-phenylethyl chloride for 48 hours on the water-bath, and the partly solid reaction product was shaken with water and ether. The ethereal layer contained no bases, but only an olefinic substance together with the excess of β-phenylethyl chloride. The residue obtained on evaporation was treated with bromine, and the solid dibromide identified as *p*-nitrostyrene dibromide by direct comparison with a genuine specimen and by oxidation by means of permanganate to *p*-nitrobenzoic acid. No styrene dibromide could be found.

The aqueous solution was basified and extracted with ether, and the ethereal solution precipitated by picric acid dissolved in benzene. The picrates (10 g.) consisted of a mixture of β-phenylethyldimethylammonium picrate (about one-third) and *p*-nitro-β-phenylethyldimethylammonium picrate (about two-thirds), which were readily separated by crystallisation from alcohol containing 10% of acetone, the former salt remaining in the solution.

The alkaline aqueous solution was filtered, neutralised, and precipitated with aqueous sodium picrate; the crude *di*(β-*phenylethyl*)*dimethylammonium picrate* thus obtained crystallised from alcohol in orange-yellow plates (8 g.), m. p. 111—112° (Found: C, 60·5; H, 5·4; N, 11·8. $C_{24}H_{26}O_7N_4$ requires C, 59·8; H, 5·4; N, 11·6%). This compound was also prepared by heating 33% alcoholic dimethylamine solution with excess of β-phenylethyl chloride in a sealed tube at 90° for 16 hours. The *hydrochloride* was thus obtained in good yield. It is readily soluble in water, alcohol, acetone, and chloroform, and separates from the last or from acetone–benzene in colourless needles, m. p. 70°. It is insoluble in ether and benzene and is not hygroscopic. On treatment with sodium picrate solution the above picrate is formed.

*Decomposition of di*(β-*phenylethyl*)*dimethylammonium hydroxide.* An aqueous solution of the hydroxide rapidly decomposed when boiled, the products being styrene, which was identified as its bromide, and β-phenylethyldimethylamine, identified as picrate.

β-*p*-Nitrophenylethyldimethylamine was prepared by heating β-*p*-nitrophenylethylamine hydrochloride (9 g.) with 20 c.c. of 40% formaldehyde under pressure at 135°. The chloride thus obtained was converted into the oxalate, which was twice crystallised from 95% alcohol (yield of pure oxalate, 10·5 g.). The more rapid but less economical method of heating the primary hydrochloride (2 parts) with paraformaldehyde (1 part) for 1 hour in an open flask at 150° was also employed; complex condensation products were formed which impaired the yield.

(IV). *β-Aminodimethyldiethylammonium Hydroxide, β-Dimethylaminodimethyldiethylammonium Hydroxide, s-Tetramethyldiethylethylenediammonium Dihydroxide, Hexamethylethylenediammonium Dihydroxide, and their Intermediates.*—The first of these bases, $(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2Et)^{\cdot}\,OH'$, was prepared by hydrolysis of the condensation product, $\{C_6H_4{:}(CO)_2{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2Et\}^{\cdot}\,Br'$, of phthal-β-bromoethylimide and dimethylethylamine.

Phthal-β-bromoethylimide (10 g.), absolute alcohol (15 c.c.), and 25% alcoholic dimethylethylamine (11 g. of solution) were warmed together in a sealed tube with frequent shaking until a homogeneous liquid resulted. The tube was then heated for 6 hours at 120°, and opened while still warm, since, on cooling, a very stiff cake of crystals is obtained. After being washed with absolute alcohol, the *β-phthalimidodimethyldiethylammonium bromide* was almost pure, m. p. 280° (decomp.); the yield (about 60%) could be slightly increased by working up the alcoholic filtrate. The salt is extremely soluble in water and is conveniently crystallised by dissolving it in a little water, warming, and adding much absolute alcohol; it then separates in pearly leaflets (Found: C, 51·4; H, 6·2. $C_{14}H_{19}O_2N_2Br$ requires C, 51·4; H, 5·8%).

The bromide was boiled with 20% hydrochloric acid (6 parts) for 6 hours and the cooled solution was filtered from phthalic acid and evaporated to dryness. A solution of the residue in a little water was filtered from a small quantity of phthalic acid and treated with sodium picrate solution. *Dimethylethylethylenediammonium dipicrate*, $\{NH_3{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2Et\}^{\cdot\cdot}\{O{\cdot}C_6H_2(NO_2)_3\}'_2$, separates from hot water in well-formed, lemon-yellow leaflets, m. p. 198° (decomp.) (Found: C, 37·3; H, 4·1. $C_{18}H_{22}O_{14}N_8$ requires C, 37·6; H, 3·8%).

Tetramethylethylenediamine has been prepared by Freund and Michaels (*Ber.*, 1897, **30**, 1385) from ethylene dibromide and dimethylamine. The bromide (14 g.) and the base (20 g. of a 33% alcoholic solution) were heated for 3 hours at 100° under pressure, and the salt was washed with alcohol and distilled with potassium hydroxide. The base was dried by distillations over potassium hydroxide and barium oxide (yield 5·6 g.).

Attempts to prepare the same compound by methylating ethylenediamine with paraformaldehyde were unsuccessful when free ethylenediamine or its hydrochloride was used, but succeeded with the sulphate. The yield is only 40%, but the method is rapid and convenient. A solution of ethylenediamine (40 g.) in absolute alcohol was neutralised with concentrated sulphuric acid and the precipitated salt was collected and dried. An intimate mixture of this with paraformaldehyde (90 g.) was heated under reflux, melting and frothing commencing at 90°. The internal temperature was maintained between 130° and 140° for 4 hours. After cooling, the product was mixed with concentrated aqueous potassium hydroxide and distilled (b. p. about 95°), and the distillate was dried with solid potassium hydroxide and distilled over barium oxide; the main portion boiled at 121—122·5°. The dipicrate is sparingly soluble, but separates from aqueous acetone in yellow needles, m. p. 263° (decomp., becoming brown at 250°) (Knorr, *Ber.*, 1904, **37**, 3509, gives 252° as the m. p. of an unrecrystallised specimen).

An ethereal solution of tetramethylethylenediamine was allowed to react with ethyl iodide (1 mol.) for several days. Small white needles, a liquid, and large needles were successively deposited. The precipitate was washed with ether by decantation, exposed in a desiccator until completely solid, and then crystallised from hot alcohol. s-*Tetramethyldiethylethylenediammonium di-iodide* separated in large, colourless needles, which lost their lustre in a desiccator or in air; m. p. 233° (decomp.) (Found: C, 28·1; H, 6·4. $C_{10}H_{26}N_2I_2$ requires C, 28·0; H, 6·1%). The salt is readily soluble in water and gives a neutral reaction. On addition of aqueous sodium picrate, the *dipicrate* is precipitated, which separates from aqueous acetone–alcohol in small, flattened needles, m. p. 261° (decomp.) (Found: C, 42·2; H, 4·9. $C_{22}H_{30}O_{14}N_8$ requires C, 41·9; H, 4·7%).

The alcoholic filtrate obtained in the preparation of the di-iodide was evaporated in a vacuum to a thick syrup, which had a strongly alkaline reaction and was soluble in chloroform. Its solution in alcohol was mixed with alcoholic hydrogen chloride and the pale brown hygroscopic salt was collected and converted into the picrate, which, after crystallisation from aqueous acetone–alcohol, had m. p. 212—214°. The same picrate was obtained when tetramethylethylenediamine was allowed to react with a small quantity of ethyl iodide without a solvent for 48 hours at the ordinary temperature. The solid iodide, which was collected and washed with ether, was hygroscopic and its aqueous solution had an alkaline reaction. The addition of aqueous sodium picrate yielded a precipitate having m. p. 210—214°. A similar but less pure product, m. p. 207—214°, was obtained in small amount, along with a large quantity of the diammonium iodide, m. p. 233°, when excess of ethyl iodide was employed. The m. p. (212—214°) of β-*dimethylaminodimethyldiethylammonium picrate* is depressed to about 205° by admixture with the dipicrate (m. p. 261°), but analysis indicates the presence of a small amount of this salt which we were unable to remove (Found : C, 44·6; H, 5·8. $C_{14}H_{23}O_7N_5$ requires C, 45·0; H, 6·2%).

*Hexamethylethylenediammonium dipicrate*, orange-yellow needles, m. p. 285° (decomp.), was prepared by mixing tetramethylethylenediamine with trinitroanisole (2 mols.) in benzene solution. It was crystallised from a large volume of hot water (Found : C, 40·1; H, 4·4. $C_{20}H_{26}O_{14}N_8$ requires C, 39·9; H, 4·3%).

*Decomposition of* β-*aminodimethyldiethylammonium hydroxide.* The aqueous solution obtained by shaking a suspension of the picrate in hydrochloric acid with benzene was concentrated to a syrup, diluted, and decomposed with water and excess of silver oxide; the filtered solution was then distilled in the usual apparatus. A portion of the solution in the 3*N*-hydrochloric acid trap was distilled and the first fraction of distillate, which strongly reduced Fehling's solution, was treated with *p*-nitrophenylhydrazine, acetaldehyde-*p*-nitrophenylhydrazone being obtained.

The solution in the bromine trap was mixed with ice, decolorised with sulphur dioxide, rendered alkaline, and extracted with light petroleum; ethylene dibromide, b. p. 131°, was then obtained in 45% yield (Found : C, 12·9; H, 2·3; Br, 84·9. Calc. : C, 12·8; H, 2·1; Br, 85·1%).

The acid solutions were evaporated to dryness and the hygroscopic residue was mixed with solid potassium hydroxide and distilled at 60°. The distillate was collected in ether and treated with picric acid in benzene, and the precipitate was crystallised twice from alcohol, pure dimethylethylammonium picrate being obtained (yield 19%). The residual bases were then completely distilled and boiled with alcoholic methyl sulphate and anhydrous sodium carbonate for 2 hours. On adding water, boiling off the alcohol, and adding sodium picrate solution in excess, a precipitate was obtained which, after two crystallisations from boiling water, yielded pure hexamethylethylenediammonium dipicrate, identical with the specimen described above (yield 30%).

*Decomposition of* β-*dimethylaminodimethyldiethylammonium hydroxide.* The solution of the hydroxide was prepared and distilled as in the last example, and the ethylene dibromide (yield 48%) isolated in the same way. The bases were also worked up in a similar manner, excepting that the tetramethylethylenediamine was purified through its sparingly soluble picrate and was not converted into the quaternary compound. The yield of dimethylethylammonium picrate was 20% and of the diammonium dipicrate 28%.

(V). β-*Hydroxydimethyldiethylammonium Hydroxide.*—β-Hydroxydimethylethylamine was prepared by a modification of Knorr and

Matthes's method (*Ber.*, 1901, **34**, 3482). Ethylene oxide (20 g.) was added to 64 g. of 33% aqueous dimethylamine previously diluted with ice-water. The product was distilled, the first 20 c.c. being rejected, up to 136°, and the distillate was saturated with potassium hydroxide and extracted with ether. The extract was dried with sodium sulphate and with solid potassium hydroxide, and the ether distilled up to 40°. Barium oxide was then added, and the aminohydrin distilled, b. p. 130—133°.

The reaction with ethyl iodide takes place on warming in ethereal solution, the product separating in colourless needles, which may be accompanied by a viscous liquid if the hydroxy-base used is not perfectly dry. In the latter case the liquid product may be caused to solidify by desiccation. β-*Hydroxydimethyldiethylammonium iodide* is excessively soluble in water and alcohol and is very hygroscopic. The *picrate* separates from water or alcohol in long needles, m. p. 237—239°. It is easily soluble in hot water and alcohol and very easily soluble in acetone (Found : C, 42·0; H, 5·2; N, 16·4. $C_{12}H_{18}O_8N_4$ requires C, 41·6; H, 5·2; N, 16·2%). It forms two modifications, the more stable having m. p. 258°.

*Distillation of the hydroxide.* The quaternary hydroxide prepared from the iodide and silver oxide was distilled as usual. Much frothing occurred. Acetaldehyde was identified through its *p*-nitrophenylhydrazone, as in Section IV, and ethylene as its dibromide (yield 37%). The acid solution was evaporated and the residue was covered with ether and basified with solid potassium hydroxide. The ethereal extract was dried with sodium sulphate and distilled over barium oxide. The main portion of the ethereal distillate, on treatment with a benzene solution of picric acid, yielded pure dimethylethylammonium picrate. The last portion, which was collected separately, on similar treatment gave a mixture of picrates (m. p. 190—195°) from which the same pure picrate (m. p. 202—203°) was obtained by crystallisation from alcohol (total yield, 26%). The β-hydroxydimethylethylamine passed over at about 100—135° and was purified through its picrate (Knorr and Matthes, *loc. cit.*).

(VI). β-*Chlorodimethyldiethylammonium Hydroxide.*—β-Chlorodimethylethylamine was prepared by Knorr (*loc. cit.*) by heating β-hydroxydimethylethylamine with fuming hydrochloric acid at 180°. The following process is less laborious.

A chloroform solution of β-hydroxydimethylethylamine, obtained from 30 g. of ethylene oxide as described in Section V, was well cooled and slowly treated with thionyl chloride until the two liquid layers at first produced became one. The solution was then heated under reflux, and the crystals, which commenced to separate after

15 minutes, were collected after the mixture had boiled for 2 hours and cooled. They were washed with a little chloroform and dried in a desiccator. In this way, 33 g. of almost pure β-chlorodimethylethylammonium chloride were obtained in colourless, hygroscopic needles, m. p. 200°. The thionyl chloride filtrate was distilled, and the brown mass of crystals was washed with ether and crystallised from a little absolute alcohol (yield, 6 g.; m. p. 196°). The corresponding *picrate* separated from 95% alcohol in large leaflets, m. p. 126—127° (Found : C, 36·1; H, 4·3. $C_{10}H_{13}O_7N_4Cl$ requires C, 35·7; H, 3·9%).

An aqueous solution of the above chloride (30 g.) was mixed with concentrated potassium hydroxide, and the base extracted with ether. Most of the ether was evaporated and the concentrated ethereal solution was warmed for several hours with excess of ethyl iodide. The crystalline product was extracted with hot alcohol, which left undissolved a small amount of tetramethylpiperazinium dichloride (m. p. 304°, decomp.), and the β-*chlorodimethyldiethylammonium iodide*, which separated, on cooling, in needles, m. p. 198° (Found : C, 27·2; H, 5·7. $C_6H_{15}NClI$ requires C, 27·3; H, 5·7%), was converted into the *picrate* by precipitation from aqueous solution with sodium picrate. This salt forms long, transparent, yellow needles, m. p. 192—193° (Found : C, 39·2; H, 4·8. $C_{12}H_{17}O_7N_4Cl$ requires C, 39·5; H, 4·7%).

*Decomposition of* β-*chlorodimethyldiethylammonium hydroxide.* The hydroxide appeared to be stable in boiling aqueous solution, but as soon as the water was driven off a violent reaction set in. The main basic product was dimethylethylamine, which was isolated as picrate in the usual way. Only traces of gaseous olefin were collected in the bromine, and in the distilling flask an amorphous product remained which contained chlorine and nitrogen but was insoluble in the usual solvents.

(VII). *Trimethyl*-n-*propylammonium Hydroxide.*—Collie and Schryver showed that the main products of decomposition were trimethylamine and propylene; analytical data indicated that dimethylpropylamine also was produced in small amount. The solution obtained by treating trimethyl-*n*-propylammonium iodide with silver oxide and water was concentrated by distillation (the distillate did not contain more than a trace of trimethylamine) and then distilled through the usual series of traps. The yields of methyl alcohol, isolated as methyl *p*-nitrobenzoate, ranged from 4 to 7%. Experiments with artificially prepared, dilute solutions of methyl alcohol showed that this method of isolation is by no means quantitative, and hence the amount of methyl alcohol formed must have been considerably greater than that stated above. Nearly pure propylene dibromide, b. p. 134—141°, the main part having b. p. 139—140° (Found : C, 18·1 ; H, 2·9 ; Br, 79·2. Calc. : C, 17·8 ; H, 3·0 ; Br, 79·2%), was obtained in 81% yield. Preliminary experiments showed that the absorption of the olefin was quantitative and took place entirely in the first bromine trap. After successive treatment with ice, sulphur dioxide and sodium hydroxide (slight excess), the bulk of the bromide was run off, and the remaining trace extracted with a little petroleum (b. p. 40—45°). The mixture of bromide and petroleum was dried with calcium chloride and distilled through a cooled column. The yield recorded above includes a correction (2·6%) for the weight of vapour filling the flask at the boiling point up to the level of the side arm. Our practice in this and similar experiments was to calculate this correction from the gas laws and also weigh the drop of liquid which condensed in the flask on cooling; usually both estimates agreed, but in the event of disagreement, the smaller value was regarded as the correction. A small correction is also applied for the volatility of the bromide in the ligroin vapour. The yield of mixed quaternary picrates obtained from the mixed bases and trinitroanisole was 89% (m. p. about 190°) and a single crystallisation from 95% alcohol yielded 78% (*i.e.*, 87·5% of the mixture) of pure tetramethylammonium picrate (Found : C, 40·4, 40·2 ; H, 4·7, 4·9 ; N, 18·5. Calc. for tetramethylammonium picrate : C, 39·7 ; H, 4·6 ; N, 18·5. Calc. for trimethylpropylammonium picrate : C, 43·7 ; H, 5·5 ; N, 17·0%). From the carbon content, the mixture contains 15% of trimethylpropylammonium picrate, *i.e.*, 14 molecules %, which agrees with the yield of propylene dibromide to within the limits of analytical accuracy. A small quantity of trimethylpropylammonium picrate was isolated from the residues of the crystallisation, as follows : the alcoholic mother-liquors were evaporated and the residue was boiled for a short time with benzene containing 5—10% of acetone, in which mixture the tetramethylammonium salt is scarcely soluble. The filtered solution yielded leaflets on cooling, which, after two crystallisations from water and two from methyl alcohol, gave stout, yellow crystals, m. p. 195—196°, consisting of pure *trimethyl*-n-*propylammonium picrate* (Found : C, 43·5 ; H, 5·6 ; N, 16·7%). This salt is much paler in colour than the tetramethylammonium salt and the progress of the separation can to some extent be followed visually. In another experiment, 6% of pure *dimethyl*-n-*propylamine*, b. p. 65—66°, was isolated by distillation of the mixed tertiary bases first over barium oxide and then over sodium (identified as picrate).

(VIII). *Trimethyl*-n-*butylammonium Hydroxide.*—These experiments were carried out in precisely the same way as those described in Section VII. We isolated 12—14% of methyl *p*-nitrobenzoate and, taking precautions to avoid loss (above), 75% (corr.) of almost pure αβ-dibromobutane, b. p. 160—165°. The carbon content of the mixed picrates (yield 93%) obtained by treating the basic product with trinitroanisole indicated the presence of 23% of trimethyl-*n*-butylammonium picrate, *i.e.*, 21 molecules %, in fair agreement with the estimate based on the yield of dibromobutane.

These results differ considerably from those of von Braun (*loc. cit.*), who claims to have obtained 50% of dried and fully rectified dimethyl-*n*-butylamine, b. p. 96°. Working on the same scale (31 g. of trimethyl-*n*-butylammonium iodide) and dehydrating the mixed bases with potash and with metallic sodium as he recommends, we obtained only 1·65 g., *i.e.*, 13%, of almost pure butyl base, b. p. 93—96°. It is difficult to avoid losses in the isolation of this substance when working on so small a scale, but it is evident from the data recorded above that von Braun's yield is much too high.

(IX). *Trimethyl*-sec.-*butylammonium Hydroxide.*—*sec.*-Butylamine was methylated with excess of methyl iodide in moist ether to which successive quantities of silver oxide were added. After addition of water and filtration, the aqueous layer was extracted with ether, titrated, and distilled. The yield of αβ-dibromobutane was about 65%, and the basic fraction consisted very largely of trimethylamine and did not contain an isolable quantity of dimethyl-*sec.*-butylamine. A portion of the liquid obtained on distilling the dilute hydrochloric acid solution in which the basic decomposition products had been collected was turbid and had the odour of *sec.*-butyl alcohol, and the methyl *p*-nitrobenzoate, obtained in very small amount from the early fractions of the distillate, was sticky, probably owing to the presence of the butyl ester. On account of the limited quantity we were able only to drain the crude methyl ester and crystallise it once, but the m. p. (88—91°) of the specimen so obtained was raised by admixture with pure methyl *p*-nitrobenzoate.

(X). *Trimethyl*iso*butylammonium Hydroxide.*—These experiments were carried out like those described in Sections VII and VIII, but a slight complication arose owing to the fact that, when the evolved *iso*butylene was passed into ice-cooled bromine, not only addition, but also a little substitution occurred with the production of hydrogen bromide. Therefore, on distilling the bromide, in addition to a considerable quantity (usually about 50%) of almost pure αβ-dibromo*iso*butane, b. p. 147—153° (Found: C, 22·4; H, 3·9. Calc.: C, 22·2; H, 3·7%), a less volatile portion was obtained having a higher proportion of bromine and lower proportions of carbon and hydrogen than correspond with the formula $C_4H_8Br_2$. This was weighed ($x$ grams) and analysed (C, $p$%), and the corresponding weight of *iso*butylene taken as 0·0117 $px$. The mean of three concordant estimates of the total quantity of *iso*butylene produced was 63%. Methyl alcohol was qualitatively identified in the usual way (17% of methyl *p*-nitrobenzoate isolated). The basic fraction consisted mainly of trimethylamine, but also contained *dimethyl*iso*butylamine* (Found: C, 71·1; H, 15·0. $C_6H_{15}N$ requires C, 71·3; H, 14·85%), 20—25% of which was isolable in a pure condition (b. p. 80—81°; distilled over sodium). *Dimethyl*iso*butylammonium picrate* separates from methyl alcohol in canary-yellow prisms, m. p. 124° (Found: C, 43·7; H, 5·7. $C_{12}H_{18}O_7N_4$ requires C, 43·7; H, 5·5%), and *trimethyl*iso*butylammonium picrate*, prepared from the tertiary base and trinitroanisole, crystallises from water in orange-yellow needles, m. p. 173—174° (Found: C, 45·5; H, 5·9. $C_{13}H_{20}O_7N_4$ requires C, 45·4; H, 5·8%).

These results differ from those recorded by Collie and Schryver (*loc. cit.*), who obtained only traces of olefin, whilst dimethyl*iso*butylamine was their sole basic product.

(XI). *Trimethyl*-tert.-*butylammonium Hydroxide.*—These experiments were carried out like those in Section IX, with comparable results, excepting that some substitution occurred in the bromine solution. Traces of methyl alcohol were detected, but the precipitated nitrobenzoic ester was oily and could not be fully purified. From the fact that on distilling the dilute hydrochloric acid solution there was an arrest at 80° we infer the probable presence of *tert.*-butyl alcohol. Methylation of the basic fraction with trinitroanisole showed that trimethylamine was the principal constituent.

(XII). *Trimethyl*-sec.-*amylammonium Hydroxide.*—The procedure and results were similar to those of the preceding section. Traces of impure methyl *p*-nitrobenzoate, m. p. 85—90°, were obtained, together with αβ-dibromopentane, b. p. 185—190°, and trimethylamine. The formation of *n-sec.*-amyl alcohol was observed (compare Section IX), but it was not isolated. The tertiary base was identified by conversion into tetramethylammonium picrate.

(XIII). *Trimethyl*-β-*ethyl*-n-*butylammonium Hydroxide.*—β-Ethyl-*n*-butylamine (ψ-hexylamine) was prepared as recommended by Freund and Hermann (*Ber.*, 1890, **23**, 192), and the fraction, b. p. 120—123° (Found: C, 71·0; H, 15·0. Calc.: C, 71·3; H, 14·85%), methylated as described in Section IX. A considerable yield (30%) of methyl *p*-nitrobenzoate was obtained. Substitution occurred in the bromine solution, as was shown by the production of hydrogen bromide, and therefore, since the quantity of material was rather limited, the mixed bromides were not distilled, but were analysed (Found: C, 28·3; H, 4·6%), and the weight of olefin was calculated from the carbon content by the formula 0·0117 $px$, giving the value 43% of the theoretical. This figure was confirmed by analysis of the mixed picrates (yield 94%) obtained by treating the basic fraction with trinitroanisole (Found: C, 45·0; H, 5·8. Calc. for tetramethylammonium picrate: C, 39·7; H, 4·6. Calc. for trimethylhexylammonium picrate: C, 48·4; H, 6·4%. Hence, proportion of tetramethylammonium picrate = 39%, *i.e.*, 43 molecules %).

(XIV). *Trimethyl-β-*n*-propyl-*n*-amylammonium Hydroxide.*—The primary base, prepared as in the preceding case *via* di-*n*-propylacetonitrile, had b. p. 163—165° (Errera, *Gazzetta*, 1896, **26**, ii, 246, gives b. p. 167° corr.). The yield of methyl *p*-nitrobenzoate was 39%. The yield of olefin determined as in the preceding experiment was 31%, and analysis of the mixed quaternary picrates indicated the presence of 29 molecules % of tetramethylammonium picrate.

(XV). *Trimethyl-*n*-propylammonium Phenoxide.*—The quaternary iodide was converted into the hydroxide, the solution of which was concentrated until it *began* to decompose. (This point is readily ascertained from the fact that the steam entering the first acid trap is not quite completely condensed, minute residual bubbles reaching the surface.) Phenol was then added (1·05 equivs.). The incipient decomposition then ceased and a further quantity of water had to be driven off, and the temperature raised, before it recommenced, indicating the greater stability of the phenoxide than the hydroxide. The solution was distilled to dryness, the anisole collecting as an oil in the first hydrochloric acid trap. It was extracted with light petroleum, washed with sodium hydroxide and distilled (yield, 65%), b. p. 153—156° (Found: C, 77·7; H, 7·5. Calc.: C, 77·8; H, 7·4%). The bases were converted into the quaternary picrates with trinitroanisole (yield 93%), and analysis of the mixture indicated that trimethyl-*n*-propylammonium picrate and tetramethylammonium picrate were present in the proportion 3 : 1. Both picrates were isolated by crystallisation as described above. The yield of nearly pure propylene dibromide, b. p. 135—141°, was 15%.

(XVI). *Trimethyl-*n*-propylammonium Carbonate.*—The hydroxide solution was saturated with pure carbon dioxide and distilled as usual. Methyl alcohol was formed in considerable quantity and isolated as the *p*-nitrobenzoate. The yield of propylene dibromide was 26% (uncorr.). A portion of the hydrochloric acid solution was basified in presence of ether, and the picrates (m. p. 110—115°)

precipitated with ethereal picric acid. They were dissolved in hot benzene, and, a certain time having been allowed for crystallisation, the still warm solution was diluted to twice its volume and at once filtered. The residue, after three crystallisations from alcohol, yielded pure trimethylammonium picrate, m. p. 215—216°. On evaporating the benzene solution and crystallising the residue repeatedly from ethyl acetate, pure dimethyl-*n*-propylammonium picrate, m. p. 108—109°, was obtained. Another portion of the acid solution was basified under ether, and the bases were methylated with trinitroanisole (yield 92%). Tetramethylammonium picrate, m. p. 306°, was obtained by crystallisation from alcohol, and trimethyl-*n*-propylammonium picrate, m. p. 194—195°, was isolated from the mother-liquors as previously described. Analyses of the mixed tertiary and quaternary salts indicated the proportion 3 : 1, the propyl derivatives preponderating.

(XVII). *Trimethyl*-n-*propylammonium* m-*Nitrophenoxide*.—This experiment was carried out in the same way as the preceding one, except that *m*-nitrophenol was added in place of phenol. *m*-Nitroanisole, m. p. 37—38°, was obtained in 89% yield by extracting the hydrochloric acid solution with ether, washing the extract with alkali, and evaporating it. A little olefin bromide was produced, but it was not enough to distil, and the base consisted almost wholly of *dimethyl*-n-*propylamine*, 84% of which was obtained in a pure condition (b. p. 65—66°; distilled over sodium) (Found : C, 68·8; H, 15·0. $C_5H_{13}N$ requires C, 69·0; H, 14·9%).

(XVIII). *Trimethyl*-n-*propylammonium Acetate*.—The hydroxide solution was exactly neutralised with acetic acid and distilled. Very little gas passed into the bromine, and, on removing the excess of halogen, only a few drops of oil, insufficient for distillation, remained. Methyl acetate was obtained in quantity by distilling the hydrochloric acid solution and redistilling the first portion of the distillate over calcium chloride; it was identified by its odour, boiling point, and by saponification, the methyl alcohol being characterised by means of its *p*-nitrobenzoate. The picrate obtained from the basic product had m. p. 104—106°, and 2·50 g., on crystallising from ethyl acetate, gave 2·25 g. of pure dimethylpropylammonium picrate, m. p. 107—108·5°. The quaternary picrates obtained by methylating the bases with trinitroanisole had m. p. 204—206°. Several crystallisations from water lowered this m. p. to 195—196°, the m. p. of pure trimethyl-*n*-propylammonium picrate. Since admixture with tetramethylammonium picrate raises the m. p. of trimethyl-*n*-propylammonium picrate, this is the behaviour to be expected if the original mixture contained a small proportion of tetramethylammonium picrate; the colour of the mixed salts also suggested the presence of a small amount of this substance, but we were not able to isolate it. Artificial mixtures of trimethyl-*n*-propylammonium picrate and tetramethylammonium picrate containing 9—10% of the latter behaved in all respects similarly, and we have little doubt that a small proportion of tetramethylammonium picrate was contained in the product obtained from the bases formed by decomposition of trimethyl-*n*-propylammonium acetate.

(XIX). *Trimethyl-*n*-propylammonium chloride* was prepared and distilled in the same way as the acetate. The yield of propylene dibromide, b. p. 139—140°, was 10% (uncorr.). The quaternary picrates obtained from the basic decomposition products and trinitroanisole had m. p. 213—222°, and on crystallisation from 95% alcohol yielded, first, pure tetramethylammonium picrate and then a mixture. When the latter *began* to be deposited, the solution was diluted with warm alcohol and filtered. The residue obtained on evaporating the filtrate, on repeated crystallisation from water, yielded trimethyl-*n*-propylammonium picrate, m. p. 195—196°. The non-volatile residue remaining in the flask consisted of a mixture of the chlorides of trimethylamine and dimethyl-*n*-propylamine, and on methylating the liberated bases, the corresponding quaternary picrates were obtained.

(XX). *Trimethyl-*n*-propylammonium Iodide.*—The results were comparable in all respects with those recorded in the preceding paragraph, except that the yield of propylene dibromide (13%) was a little greater.

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