DECOMPOSITION OF QUATERNARY AMMONIUM BASES AND OF XANTHATE ESTERS

A Thesis

by

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CLAIM TO ORIGINAL RESEARCH

Pinacolyltrimethylammonium hydroxide has been found to yield on decomposition at both 30° in vacuo, and at 100-160°, a single pure olefin, tert.-butylethylene. This is the first time the mechanism of Ingold and co-workers for such decompositions has been tested in a convincing way. The absence of rearranged products, and of saturated or cyclic hydrocarbons indicates unequivocally that the decomposition proceeds, not through free radical formation, but by expulsion of a proton, probably induced by preliminary hydrogen bonding, followed by rupture of the carbon-nitrogen bond.

This same mechanism has been successfully extended to the decomposition of xanthate esters.

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Quaternary Ammonium Hydroxides

Among the numerous methods in organic chemistry whereby one compound may be changed into another, a process consisting essentially in the elimination of certain atoms or groups of atoms from a larger molecule to produce a smaller one is remarkably common.

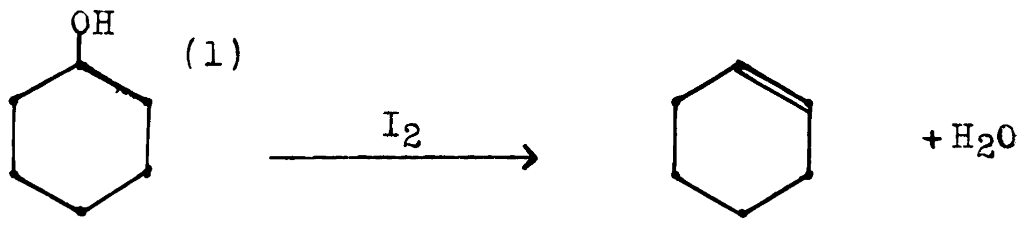
As an illustration of the reaction, one may consider the equation:

$$RA.RB \longrightarrow R{=}R + A.B$$

in which the organic compound has eliminated, either spontaneously or under the influence of some reagent, a part of itself, AB, and has been reduced to a smaller unsaturated molecule, R=R. A few simple specific cases are represented by the following equations:

$$CH_3CH_2Cl \xrightarrow[KOH]{alcoholic} CH_2{=}CH_2 + HCl$$

(1)



More complex instances are represented by pinacolyl alcohol, which as Whitmore (2) has shown, using a phosphoric acid catalyst, is dehydrated with the production of only 3% of the unrearranged olefin, tert.-butylethylene, and 61% and 31% respectively, of the rearranged

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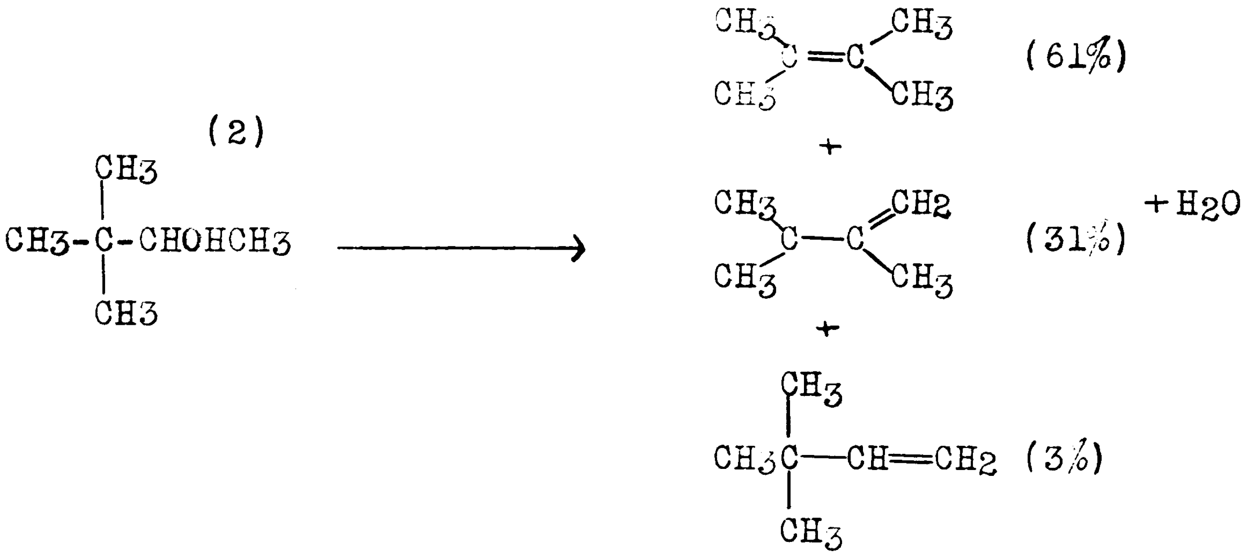
(1) Hibbert, H. J. Amer. Chem. Soc. 37 1748-63 (1915).
(2) Whitmore, F.C., Meunier, P.L. J. Amer. Chem. Soc. 55 3721-2 (1933).

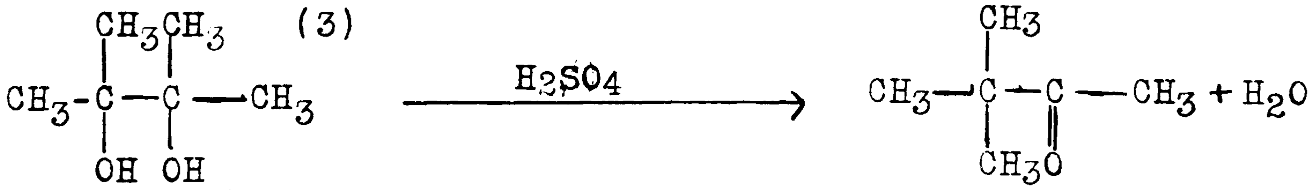
products, tetramethylethylene, and unsym.-isopropylethylene.

(2)

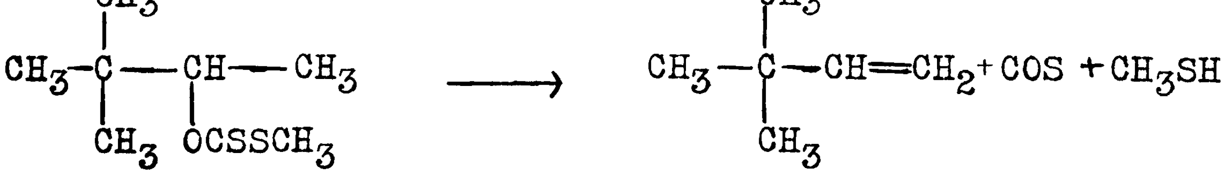


The well-known case of the dehydration of pinacol is another instance of the production of a rearranged carbon skeleton on the elimination of water.

(3)



That pinacolyl alcohol or its derivatives, does not always undergo rearrangement on elimination is shown by the decomposition of methylpinacolylxanthate (4), which yields tert-butylethylene exclusively.



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(2) Whitmore, F.C., Meunier P.L., J.Amer.Chem.Soc. <u>55</u> 3721-2)(1933)

(3) Fittig, R., Ann. 114 54-63(56)(1860).

(4) Fomin, V., Sochanski, N., Ber. <u>46</u> 244-8(1913). Schurman, I., Boord, C.E. J.Amer. Chem. Soc. <u>55</u>, 4930-35 (1933).

So too, bornyltrimethylammonium hydroxide (4a) on elimination of water and trimethylamine, gives practically pure bornylene, whereas the dehydration of borneol by other methods almost invariably leads entirely to the rearranged product, camphene.

An immense amount of data has been accumulated on the dehydration of carbinols by a great variety of methods and reagents. But with a few exceptions including the ones noted above all these methods have been found to lead in part, if not entirely, to a rearrangement of the carbon skeleton if that is at all possible. It is therefore of considerable interest to examine the decomposition of two exceptional classes of compounds, which comprise the quaternary ammonium hydroxides (made from the amine of the corresponding carbinol), and certain organic esters, notably the xanthates, but including also dixanthates, acetates and benzoates. The yields of olefins from the pyrolysis of these latter three esters have been found, in general to be less satisfactory than those from the xanthates, and it is to the xanthates that most attention will be directed.

To cite one example of dehydration by pyrolysis of acetates there is the work of Whitmore and Rothrock (5)

(4a) Shriner, R.L., Sutherland, H., J.Amer.Chem.Soc., <u>60</u> 1314-20 (1938)

(5) Whitmore, F.C., Rothrock, H.S., J.Amer.Chem.Soc., 55 1106-09 (1933).

on the acetate of pinacolyl alcohol. By distilling this substance over porous tile in a pyrex tube heated to 300°, a rather small yield of the unrearranged hydrocarbon, tert.-butylethylene was obtained. The experimental difficulties however, are such as to render the method unsuitable for the convenient preparation of tert-butylethylene.

An endeavour will be made to find wherein the type of elimination reaction illustrated by the decomposition of quaternary ammonium hydroxides and of xanthates differs in mechanism from those other elimination reactions which result in a rearrangement of the organic residue. It is true that in a few instances, to be considered later, that rearranged products have been observed even from these compounds; in nearly all cases however, the rearrangement may be shown to be the result of secondary reactions of the original, unrearranged product, brought about by the experimental conditions.

Preparation and Properties.

During the course of investigations on "The Molecular Constitution of Volatile Organic Bases", A.W. Hofmann(6) in 1850 was able to replace step by step, one two or three equivalents of hydrogen in ammonia by a corresponding number of organic radicals, and to produce thereby a tertiary amine - in this particular case, diethylaniline.

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(6) Hofmann, A.W. Phil. Trans. 140 93-131 (106 and 122) (1850.)

Since there was then no longer any replaceable hydrogen in the base, Hofmann doubted that a further reaction would occur between ethyl bromide and diethylaniline; nevertheless, in order definitely to establish the point, he continued his investigations. At first it appeared as he expected, that there was no reaction, ethyl bromide and diethylaniline being recovered largely unchanged, either after contact for nearly a month, or after heating together in a sealed tube. But in each of these experiments there was formed in small amounts, a water soluble compound which Hofmann called a hydrobromide. In the case where aqueous solutions of the amines were heated with the halide, the presence of a hydrobromide could be explained by assuming a hydrolysis of the ethyl bromide to give ethyl alcohol and hydrogen bromide - the latter substance with diethylaniline giving the hydrobromide. But since a "hydrobromide" was also formed by the interaction of carefully dried reagents, Hofmann was forced to the conclusion that some other reaction was taking place. He had not observed at this stage that the hydrobromide formed under aqueous conditions, and which liberated diethylaniline on treatment with potassium hydroxide, was not the same as the one obtained under anhydrous conditions.

These difficulties, however were cleared up a year later in a second paper (7) on the constitution of

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(7) Hofmann, A.W. Phil. Trans. 141 357-398 (1851)

these bases. The experiments on the action of an ethyl halide on diethylaniline and on trimethylamine were repeated on a much larger scale; as before, the reaction between the dry reagents was extremely slow. But Hofmann shortly observed that by substituting ethyl iodide for ethyl bromide, the reaction proceeded in a few minutes with the production of a solid mass of white crystals, analysing for a compound formed by direct addition of ethyl iodide to trimethylamine- the first quaternary ammonium salt.

From the behaviour of the salts of other amines, Hofmann expected this one to liberate a base upon the addition of potassium hydroxide, and from its failure to do so, he precluded the possibility of its being analogous to the salts of ethyl -, diethyl -, and triethylamine. As was pointed out later (8), this difference in behaviour was more one of degree than of kind. The formation of a base from a quaternary ammonium salt:

$$R_4NX + MOH \rightleftarrows R_4NOH + MX$$

is a question of relative solubilities and the reaction goes to completion if M,X and the solvent are so chosen that all the components save MX shall be soluble. Thus, when M = potassium, X = iodine and the solvent is water, the equilibrium is largely on the left hand side of the equation. for it is the quaternary ammonium iodide rather

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(8) Walker, J., Johnston, J. J. Chem. Soc. <u>87</u> 955-961 (1905).

than the potassium iodide that is the more insoluble. As Hofmann found by making M = silver and X = iodine, or M = barium and X = $SO_4^=$, the product MX was in both cases quite insoluble in water, the equilibrium was shifted to the right, and by filtering off the MX, a solution of the hydroxide could be obtained. Should the solvent chosen be alcohol, then potassium hydroxide (9) may be used to liberate the base from the halide, for potassium iodide is comparatively insoluble in alcohol.

The usual method of preparation however, has generally been to methylate the amine with methyl iodide and potassium hydroxide to the quaternary iodide; this, in aqueous solution was then treated with silver oxide and the resulting strongly basic solution filtered through asbestos to remove the silver halide; solutions prepared in this way are frequently dark coloured, due to the presence of colloidal silver. v.Braun (10) has described the use of methyl sulphate in preparing the quaternary base. From this reagent, salts with the group $-O.SO_2\ CH_3$ were obtained, which were salted out with concentrated alkali and purified by recrystallization from chloroform and ether; they were then hydrolysed by sulphuric acid, excess acid being removed by the addition of barium hydroxide. On filtration, the sulphate,

(9) Lucius, R. Arch. Pharm. 245 246-58 (1907)
(10) v.Braun, J. and Anton, E. Ber. 64B 2865-9 (1931).

carbonate (if any) and excess hydroxide of barium were removed, leaving as before, an aqueous solution of the base. This method has the advantage of yielding a more easily filterable precipitate than is sometimes obtained by the use of silver oxide.

As Hofmann showed at the time of their discovery, the quaternary ammonium bases exhibited a marked similarity to the hydroxides of the alkali metals, and in particular to that of potassium.

Tetraethylammonium hydroxide was effective in the saponification of cocoanut oil to give a soft soap. More recently patents (11) have been taken out involving the use of quaternary ammonium hydroxides themselves as soaps and surface-active agents - this property being especially marked when one of the radicals attached to the nitrogen contained at least eight carbon atoms. Such bases (12), in addition, have foaming and wetting properties, and the ability to improve the fastness of dyes, which properties make them of value in the textile industry.

Measurements (13) of the relative strengths of nitrogen bases showed that they increased in the order: NH_4OH, $(CH_3)_3NHOH$, CH_3NH_3OH, $(CH_3)_2NH_2OH$, and $(CH_3)_4NOH$

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(11) Swiss Patent, 133,372 Chem. Abs. 24 380 (1930).
U.S.Patent,1,737,458 Chem. Abs. 24 628 (1930).
(12) Brit. Patent, 459,309 Chem. Abs. 31 3942(1937)
(13) Tinkler, C.K. J. Chem. Soc., 105 995-1002 (1914)

the latter being fully as strong a base as sodium hydroxide. Noyes (14) has shown that bases like trimethylethoxy -, and trimethylmethoxy - ammonium hydroxide are highly ionized in aqueous solution.

As is the case with carbon when surrounded by four different groups the ammonium hydroxides containing four different radicals joined to the nitrogen are optically active and may be resolved by recrystallization of their salts with optically active acids (15,16). This optical activity was strong evidence in favour of the theory that the nitrogen atom in ammonium compounds was tetrahedral, and not pyramidal.

Tetramethylammonium hydroxide resembled potassium hydroxide in that when its aqueous solution was mixed with a large excess of hydrogen peroxide (17) and evaporated to dryness in vacuum at room temperature, a yellow residue of tetramethylammonium tetroxide $\left[(CH_3)_4N\right]_2O_4$ was obtained. On addition of water or acids, oxygen was evolved, hydrogen peroxide was found to be present in the solution and the quaternary ammonium radical was recovered almost quantitatively as the iodide, a fact which showed that it had undergone practically no oxidation. With tetraethylammonium

(14) Noyes, W.A. J.Amer. Chem. Soc. 47 3025-30 (1925).
(15) Wedekind, E., Wedekind, O. Ber. 40 4450-6 (1907).
Wedekind, E. Ber. 42 303-9 (1909).
(16) Jones, H.O. Proc. Camb. Phil. Soc. 14 376-7
(17) Traube, W., Burmeister, E., Blaser, B. Ber. 60B 439-446 (1927).

hydroxide an analogous tetroxide was obtained; using smaller amounts of hydrogen peroxide analytic results obtained on the oxide so produced seemed to indicate the presence of a peroxide containing hydrogen peroxide $[(C_2H_5)_4 N]_2 O_2 \cdot H_2O_2$.

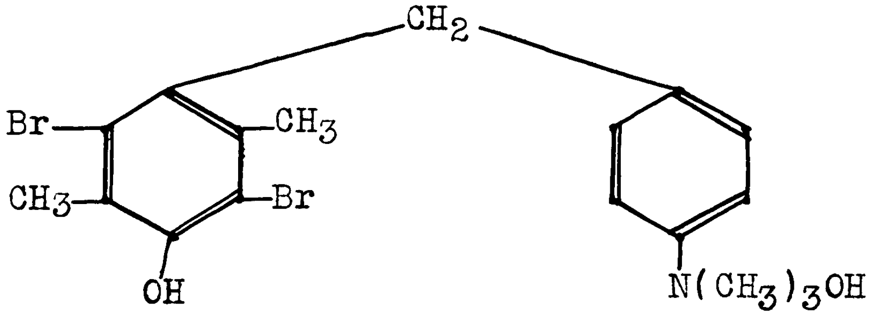
Like the "hydroxyoxides" obtained from potassium, rubidium or caesium hydroxides and ozone, tetramethyl ammonium hydroxide and ozone (18) gave a red compound for which the formula $[(CH_3)_4NOH]_2 O_2$ was proposed. This differed from the analogous compounds of the alkali series by being much more stable - probably capable of existing indefinitely at room temperature. At 75°, it decomposed smoothly to oxygen and tetramethylammonium hydroxide; water caused the evolution of oxygen and the regeneration of the original ammonium base. Only traces of hydrogen peroxide were detected, and it was shown that this was formed, not in the liberation of oxygen from the red compound, but from the oxidizing action of ozone on tetramethylammonium hydroxide.

With potassium permanganate, quaternary ammonium (19) bases like choline and acetylcholine gave betaine or trimethylamine, depending on whether the medium was acid or alkaline, respectively.

(18) Traube, W., Kuhbier, F. Ber. 62B 809-20 (1929).
(19) Lintzel, W., Fomin, S. Biochem. Z. 238 438-51 (1931).

Recently, use was made of tetramethylammonium hydroxide to obtain in excellent yield, the methyl esters of difficultly esterfied acids (20,21). The procedure consisted in dissolving the acid in methyl alcohol; titrating with a solution of pure tetramethylammonium hydroxide, using phenolphthalein as the indicator; and then removing the solvent and decomposing the residue by heat, to trimethylamine and practically pure methyl ester.

In spite of repeated attempts (23,24) to obtain quaternary ammonium bases in the crystalline, anhydrous form, only in a few cases (25) has this been possible. The stable anhydrous bases have always been complex, highly substituted compounds like 3,6 - dibromo- 4- hydroxy- 2,5- dimethyldiphenylmethane -4′ - trimethylammonium hydroxide



v.Auwers (25) showed that this existed as the free hydroxide, not in the oxide form, and reported its melting at 208°.

(20) Prelog, V., Picentamida, M. Z. Physiol. Chem. 244 56-8 (1936).
(21) Fuson, R.C., Corse, J., Horning, E.C. J. Amer. Chem. Soc. 61 1290 (1939).
(23) Crichton, D.C. J. Chem. Soc. 91 1793-97 (1907).
(24) Stewart, T.D., Aston, J.G., J. Amer. Chem. Soc. 49 1718-28 (1927).
(25) v.Auwers, K. Ann. 334 264-342 (1904).
Fourneau, E., Bull. Soc. Chim. IV 3 1141-45 (1908).
Rupe, H., Thiess, K.G., Wetter, A. Ber. 42 4287-4304 (1909)

But if the simpler hydroxides have not been obtained as stable anhydrous solids their existence in the form of well crystallized hydrates has often been reported (7, 23). Crichton, for instance, isolated tetramethylammonium hydroxide hydrate with four and with six molecules of water of crystallization; and tetraethylammonium hydroxide he obtained as the pentahydrate. All attempts to remove the water of crystallization invariably lead, not to the anhydrous base, but to decomposition of the hydroxide, and it is on this property that the great interest in these substances for the organic chemist depends.

Decomposition of quaternary bases from aliphatic amines.

The first quaternary ammonium base, the products of whose decomposition were studied was tetraethylammonium hydroxide, and Hofmann (7) found that they were water, ethylene and triethylamine

$$C_2H_5\text{-}N\text{-}(C_2H_5)_3OH \longrightarrow CH_2{=}CH_2 + H_2O + (C_2H_5)_3N$$

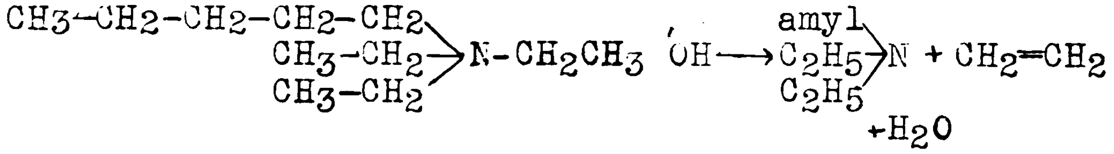
With the exception of tetramethylammonium hydroxide (26) from which no olefin formation was possible, and which decomposed according to the equation:

$$CH_3N(CH_3)_3OH \longrightarrow CH_3OH + (CH_3)_3N.$$

Hofmann found that all the other hydroxides he investigated

(26) Hofmann, A.W. Ber. 14 494-496 (1881)

yielded water, an olefin and a tertiary amine. A further generalization (27) he observed was that hydroxides of mixed quaternary ammonium compounds containing an ethyl group, invariably yielded ethylene as the unsaturated hydrocarbon. These results were later confirmed by Zander (28) who showed that not only was an olefin and no alcohol obtained from tetraethylammonium hydroxide, but that the same was true for tetrapropylammonium hydroxide. Amyltriethylammonium hydroxide for instance, decomposed according to the scheme



$$\left.\begin{array}{r}CH_3-CH_2-CH_2-CH_2-CH_2\\ CH_3-CH_2\\ CH_3-CH_2\end{array}\right\rangle N-CH_2CH_3\ ,\ OH \longrightarrow \left.\begin{array}{r}\text{amyl}\\ C_2H_5\\ C_2H_5\end{array}\right\rangle N + CH_2{=}CH_2 + H_2O$$

while with no ethyl groups present, as in tetraamylammonium hydroxide, triamyl amine and amylene were obtained.

An interesting variation in the behaviour of tetralkyl substituted ammonium bases was observed later in the case of tetrallylammonium hydroxide (29), which probably due to the fact that the allyl group is the least firmly attached of any to nitrogen, gave almost exclusively the secondary diallyl amine,

$$(CH_2{=}CH{-}CH_2)_2NH$$

(27) Hofmann, A.W. Ann. 78 282-284 (1850).
(28) Zander, A. Ann. 214 138-193 (171) (1882).
(29) Solonina, J. Russ. Phys. Chem. Soc. 38 1286 (1907).

It is probable that here the triallyl amine was first formed, as usual; the hydroxide of this $(CH_2=CH-CH_2)_3NHOH$, owing to the instability of the allyl-nitrogen bond then decomposed to the secondary amine and allyl alcohol, or the hydrocarbon.

A similar case of the production of a secondary amine in the decomposition of a quaternary ammonium hydroxide was observed by Hey & Ingold (29a), with dibenzyldiallylammonium hydroxide. This base, when heated to 170°, gave dibenzylamine, with no benzyl alcohol, or dibenzylallylamine. Part of the allyl group appeared as acrolein.

Another example among the many that Hofmann investigated was methyethylamylphenylammonium hydroxide (26) which gave, as was expected, methylamylphenylamine and ethylene. It was in this same paper and in a second (30) published shortly after that Hofmann first applied this new technique - now called exhaustive methylation and consisting of the synthesis and subsequent decomposition of the quaternary ammonium hydroxide of an amine - to the elucidation of the structure of naturally occuring nitrogen compounds. In the particular case of cyclic nitrogenous bases where exhaustive methylation results in opening of the ring and the production of an unsaturated tertiary

(29)a Hey, L., Ingold, C.K. J.Chem. Soc. 1933 66-7
(30) Hofmann, A.W. Ber. 14 659-669 (1881).

amine, the decomposition is called the Hofmann Reaction. These cases will be considered later under cyclic amines. Compounds in which one of the four alkyl groups about the nitrogen was replaced by a alkoxy group have been studied by Meisenheimer (31) later, by Stewart and Aston (24), and the products of the decomposition were found to include an aldehyde, as well as the usual trimethylamine, water, and an olefin.

The following were some of the hydroxides Meisenheimer decomposed, generally by boiling the aqueous solution.

$$[(CH_3)_3N(OCH_3)]\,OH \longrightarrow (CH_3)_3N + HCHO + H_2O$$

The isomer of this base, (not a true quaternary ammonium hydroxide) yielded an amine oxide on decomposition:

$$[(CH_3)_3NOH]\,OCH_3 \longrightarrow (CH_3)_3NO + CH_3OH$$

$$[(CH_3)_3NOCH_3]\,OC_2H_5 \longrightarrow (CH_3)_3N + HCHO + CH_3OH$$

$$[(CH_3)_3NOC_2H_5]\,OH \longrightarrow (CH_3)_3N + CH_3CHO + H_2O$$

Stewart and Aston studied the decomposition of ethoxymethyldiethylmethylammonium hydroxide under three sets of experimental conditions.

First a solution of the base was evaporated slowly (ten days) in a vacuum dessicator at room temperature; second, a similar solution was evaporated under the same conditions but somewhat more rapidly (2 days); third, a solution of the hydroxide was concentrated by distillation at atmospheric pressure. The results of the three experiments were expressed

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(31) Meisenheimer, J., Brating, K. Ann. <u>397</u> 284-300 (1913).

by the equations:

$$[(C_2H_5)_2(CH_3)NCH_2OC_2H_5]OH \begin{cases} \rightarrow C_2H_5OH + HCHO + (C_2H_5)_2NCH_3 & \text{A} \\ \rightarrow C_2H_5OH + HCHO + CH_2{=}CH_2 + C_2H_5NHCH_3 & \text{B} \end{cases}$$

In the cases of decomposition at room temperature, the reaction followed the two paths to almost exactly the same extent, 18.5% according to A, and 81.5% according to B. At higher temperatures, reaction A was favoured to the extent of at least 90 percent.

The first workers to make a comparative study of the decomposition of a series of quaternary ammonium bases were Collie and Schryver (32), whose results are summarized in the following table. It will be seen from these that, depending on the nature of the four alkyl groups attached to nitrogen, the reaction may follow one of two courses, to yield either olefin and trimethylamine, or methyl alcohol and a mixed tertiary amine. Representing the 4 alkyl (or substituted alkyl groups) by R and using the symbol r to represent the unsaturated olefin, we have

$$R_1R_2R_3R_4NOH \begin{cases} \rightarrow R_1R_2R_3N + r_4 + H_2O & \text{(A)} \\ \rightarrow R_1R_2R_4N + R_3OH & \text{(B)} \end{cases}$$

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(32) Collie, N.,Schryver, S.B. J. Chem. Soc. <u>57</u> 767-782 (1890).

				Reaction A		Reaction B	
R_1	R_2	R_3	R_4	$R_1R_2R_3N$	r_4	$R_1R_2R_4N$	R_3OH
CH_3	CH_3	CH_3	C_2H_5	$(CH_3)_3N$	$CH_2=CH_2$	0	0
"	"	"	$CH_3CH_2CH_2$	$(CH_3)_3N$	$CH_3CH=CH_2$	traces	traces
"	"	"	i-propyl	$(CH_3)_3N$	$CH_3CH=CH_2$	0	0
"	"	"	i-amyl	$(CH_3)_3N$	amylene	traces	traces
"	"	"	allyl	$(CH_3)_3N$	acrolein	"	"
"	"	"	t-amyl	$(CH_3)_3N$	amylene	"	"
"	"	"	i-butyl	traces	traces	$(CH_3)_2$(i-butyl)N	CH_3OH
"	"	"	phenyl	0	0	$(CH_3)_2(C_6H_5)N$	CH_3OH
"	"	"	benzyl	$(CH_3)_3N$	$C_6H_5CH_2OH$ + $C_6H_5-C_6H_5$	traces	traces
CH_3	C_2H_5	C_2H_5	C_2H_5	$(CH_3)(C_2H_5)_2N-C_2H_4$		0	0
"	CH_3	"	"	$(CH_3)_2(C_2H_5)N-C_2H_4$		traces	traces
C_2H_5	C_2H_5	C_2H_5	$C_6H_5CH_2$	$(C_2H_5)_3N$	$C_6H_5CH_2OH$	traces	traces

A tertiary amine of some kind always resulted from the decomposition of the hydroxide, and in cases like trimethylphenyl-, trimethylisobutyl-, and methyltriethylammonium hydroxides it becomes an excellent method for the synthesis of the mixed tertiary amine.

From the foregoing work it is evident that the case of elimination of a given radical from a quaternary ammonium hydroxide depends on the particular nature of that radical, and to obtain some comparative quantitative data, v.Braun (33) studied a large number of hydroxides of the type $RN(CH_3)_3OH$ where R was an aliphatic radical; again the results may be summarized in a table showing the nature of R and the percent of methyl alcohol from the decomposition. From the equations A and B above (page 16) it will be seen that the percent of methyl alcohol obtained is a measure of the relative amount of decomposition in the two directions - a high percentage of alcohol corresponding to a low yield of olefin. Later investigations by Ingold (33a) and v.Braun (33b) have shown that although the groups in the table appear in the correct relative order, the actual percent of decomposition to methyl alcohol is in most cases in error due to the presence of carbonates in v.Braun's original solutions. Since v.Braun's results in the table immediately following show too high a percent of quaternary hydroxide decomposing to give methyl alcohol, it is not unlikely that values obtained under the same experimental conditions (free access of carbon dioxide from the air to the solution being decomposed) and shown in later tables, are also too high. Nevertheless, experimental conditions having been uniform throughout, the relative order of the various groups is not changed and v.Braun's observations on the effect of

(33) v.Braun,J. Ann. 382 1-49 (1911).
(33a) Ingold, C.K. and Vass, C.C.N. J. Chem. Soc., 1928 3125-27.
(33b) v.Braun, J., Teuffert, W., Weissbach, K. Ann.472 121-42 (1929).

substitution on decomposition are still of interest.

Nature of R in R $N(CH_3)_3OH$	% of base yielding CH_3OH on decomposition.	
	v.Braun	Ingold & Vass (33a)
(1) C_2H_5 (32)	0	0
(2) C_3H_7 (32)	5-10	16
(3) C_4H_9	50	21
(4) C_5H_{11}	60	23
(5) C_6H_{13}	73	24
(6) C_7H_{15}	75	26
(7) C_8H_{17}	75	25
(8) $C_{16}H_{33}$	75	

v.Braun noted that when R was a lower member of the alkyl series the decomposition proceeded mainly according to equation A (p.16) to give trimethyl amine, an olefin and water. With increasing molecular weight of R, the percent of decomposition in this direction decreased in favour of that represented by equation B to produce the mixed tertiary amine and methyl alcohol. Increase of molecular weight of R beyond C_6 had little effect on the relative amounts of base decomposing in the two possible directions, but according to v.Braun, it did affect the nature of the products resulting from the small fraction of the base not decomposing according to equation A; he found that from hydroxides containing a higher alkyl group - cetyltrimethylammonium hydroxide for instance - very little cetene and water were evolved with trimethylamine, but rather, cetyl alcohol and trimethylamine. The validity of v.Braun's observations on the production of a saturated primary alcohol (other than methyl) in decompositions of this type has been questioned by Ingold and Kuriyan (33c). The earlier experiments of Ingold and co-workers on heptyl-, octyl-, and cetyl - trimethylammonium hydroxides have not enabled these authors to confirm v.Braun's statements that the quaternary bases yield some heptyl, octyl and cetyl alcohols together with the olefin; and while they do not deny that such higher alcohol formation may occur, they suggest that the statement that it does, requires additional support.

A further series of compounds - derivatives of the propyl-, butyl-, and amyltrimethylammonium hydroxides of the previous table - studied by v.Braun follows:

Quaternary hydroxide	% of base yielding CH_3OH on decomposition
(9) C_6H_5O————$(CH_2)_3N(CH_3)_3OH$	10
(10) C_6H_5O————$(CH_2)_4N(CH_3)_3OH$	55
(11) CH_3O————$(CH_2)_5N(CH_3)_3OH$	60
(12) C_6H_5O————$(CH_2)_5N(CH_3)_3OH$	60
(13) NH_2————$(CH_2)_5N(CH_3)_3OH$	60
(14) C_6H_5CONH————$(CH_2)_5N(CH_3)_3OH$	60

As may be seen by comparing hydroxide 10, above, with hydroxide 3 in the previous table (p.19), and hydroxides 11,12,13 and

(33c) Ingold, C.K., Kuriyan, K.I. J. Chem. Soc. <u>1933</u> 991-3 (991).

14 with 4, that mere increase in the molecular weight of R was of little effect on the course of the decomposition, if the extra organic residue were connected to the hydrocarbon radical by other than a C-C link. To consider a specific case, propyltrimethylammonium hydroxide, as Collie and Schryver had found, gave 5 - 10% methyl alcohol, a result that would have been predicted in the light of this observation, from v.Braun's value of 10% methyl alcohol from phenoxypropyltrimethylammonium hydroxide; here the molecular weight of R had increased, but since the added portion was joined to the original propyl group by an oxygen atom, and not a direct C-C bond, it was without influence on the course of the decomposition.

The next step was to consider the effect of moving the phenyl group in benzyltrimethylammonium hydroxide progressively further away from the nitrogen, and v.Braun obtained the following values:

		% of hydroxide decomposing to CH_3OH
(15)	$C_6H_5CH_2N(CH_3)_3OH$	very little
(16)	$C_6H_5CH_2CH_2N(CH_3)_3OH$	0%
(17)	$C_6H_5CH_2CH_2CH_2N(CH_3)_3OH$	70
(18)	$C_6H_5CH_2CH_2CH_2CH_2CH_2N(CH_3)_3OH$	75%

v.Braun concluded from these results that olefin formation in the decomposition of quaternary ammomium hydroxides was a primary step in the reaction, and did not result from the secondary dehydration of an alcohol. The manner of decomposition depended first, on the tendency of the lighter groups to be eliminated as alcohols; secondly, on the tendency, by means of elimination of water, to form olefins of symmetrical structure.

From these, and other observations of a similar nature considered later, a list of radicals arranged in order of increasing ease of elimination from a quaternary base was established: phenyl, cyclopropylmethyl, octyl, hexyl, isoamyl, methyl, butyl, isobutyl, cyclopropyl, propyl, ethyl, phenylethyl, p-nitrophenylethyl, benzyl, allyl.

The presence of an ethylenic link in the aliphatic group of the quaternary ammonium hydroxide facilitated the elimination of that group when the unsaturation was close to the nitrogen; but as the unsaturated link moved farther away, the percent of hydrocarbon formed became less and less (34). Merling (35) had shown that the quaternary hydroxides from Δ^4-pentenyldimethylamine and from Δ^5- hexenyldimethylamine both readily decomposed to yield a doubly unsaturated olefin.

$CH_2{=}CH(CH_2)_3N(CH_3)_2 \longrightarrow$ Quat. base $\longrightarrow C_5H_8 + H_2O + (CH_3)_3N$

$CH_2{=}CH(CH_2)_4N(CH_3)_2 \longrightarrow$ Quat. base $\longrightarrow C_6H_{10} + H_2O + (CH_3)_3N$

However, from the corresponding saturated ammonium hydroxides

$CH_3(CH_2)_4N(CH_3)_3OH$ and $CH_3(CH_2)_5N(CH_3)_3OH$

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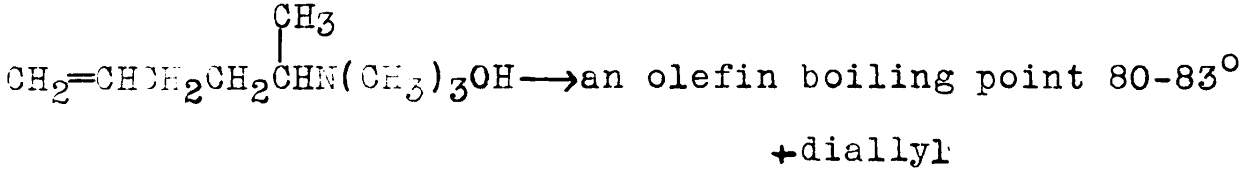
(34) v.Braun, J. Ann. <u>386</u> 273-303 (1911).
(35) Merling G. Ann. <u>264</u> 310-351 (1891).

there was obtained much less olefin and 50-60% of the mixed tertiary amine. In the C_{10} case, the loosening effect of the terminal double bond had so diminished that trimethyl- Δ^9 decenyl-ammonium hydroxide yielded no more hydrocarbon than did the corresponding saturated derivative.

It might be pointed out here that Merling obtained in addition to the expected diallyl from the decomposition of Δ^5 hexenyltrimethylammonium hydroxide, an isomeric hydrocarbon of boiling point 80-83°; from the decomposition of 1-methyl- Δ^4 pentenyltrimethylammonium hydroxide, the same two hydrocarbons were isolated



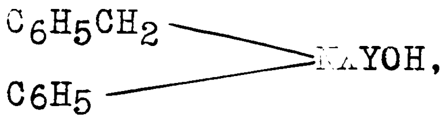
$$CH_2{=}CHCH_2CH_2\overset{CH_3}{\overset{|}{C}}HN(CH_3)_3OH \longrightarrow \text{an olefin boiling point } 80\text{-}83^{\circ} + \text{diallyl}$$

Since in the latter case, two isomers, either

$CH_2{=}CH{-}CH_2CH_2CH{=}CH_2$ diallyl, or $CH_2{=}CHCH_2CH{=}CHCH_3$, hexadiene-1,4 would be expected depending on which hydrogen in the β position to the nitrogen were lost. Merling assigned the hexadiene-1,4 structure to the hydrocarbon of boiling point 80-83°. The evidence for this structure was not particularly conclusive, and recalling the tendency of isolated double bonds in a diene to rearrange into a conjugated system, it is not improbable that Merling's 80-83° hydrocarbon is hexadiene-1,3.

Following the earlier work of Hofmann and v.Braun, other investigators have studied long series of quaternary ammonium hydroxides to find the relative ease of elimination of various radicals as olefins.

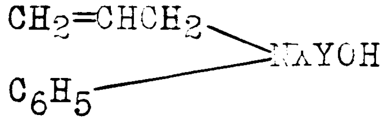
Komatsu (35a) showed that in hydroxides of the type



$$\begin{matrix} C_6H_5CH_2 \\ C_6H_5 \end{matrix} \!\!> NXYOH,$$

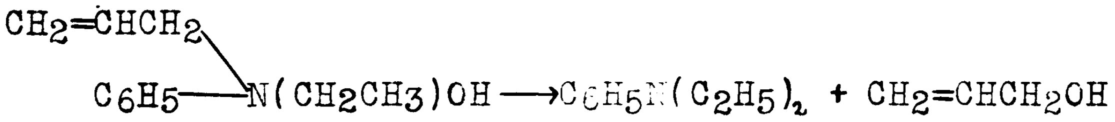
where X and Y were any other organic radical (methyl, ethyl, n-propyl, allyl, n-butyl, isobutyl, isoamyl, or benzyl,) that benzyl was always the group to be eliminated, presumably as benzyl alcohol.

In the series



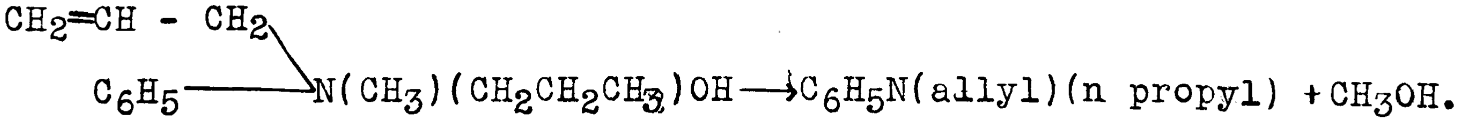
$$\begin{matrix} CH_2{=}CHCH_2 \\ C_6H_5 \end{matrix} \!\!> NXYOH$$

if X and Y were smaller than allyl, the latter underwent scission from the nitrogen, thus:



$$\begin{matrix} CH_2{=}CHCH_2 \\ C_6H_5 \end{matrix} \!\!> N(CH_2CH_3)OH \longrightarrow C_6H_5N(C_2H_5)_2 + CH_2{=}CHCH_2OH$$

If one group were larger and the other smaller than allyl, then the smaller one was removed:



$$\begin{matrix} CH_2{=}CH - CH_2 \\ C_6H_5 \end{matrix} \!\!> N(CH_3)(CH_2CH_2CH_3)OH \longrightarrow C_6H_5N(allyl)(n\ propyl) + CH_3OH.$$

Apart from these two classes, Komatsu concluded that in hydroxides of the type $R_1R_2R_3R_4NOH$, the smallest of the four groups was always left attached to nitrogen. This principle is demonstrated by the compounds in the following table, which shows the nature of the four alkyl groups in the hydroxide, and the mixed tertiary amine obtained on decomposition.

(35a) Komatsu, S. Mem. Coll. Sci. and Eng. Kyota Imp. Univ. 3 371-426 (1912). J. Chem. Soc. 104 i 39 (1913).

An exception to the general rule is the last compound (35b) in the table which gives only a little of the N-methyl mixed tertiary amine:

R_1	R_2	R_3	R_4	t-amine
C_6H_5	CH_3	C_2H_5	n-butyl	methyl n-butyl aniline
"	"	"	isoamyl	" isoamylaniline
"	"	n-propyl	isobutyl	" n-propylaniline
"	"	"	isoamyl	" " "
"	"	n-butyl	"	" isoamylaniline
$C_6H_5CH_2$	"	$C_6H_5CH_2$	"	dibenzylisoamylamine with a little methylbenzylisoamylamine

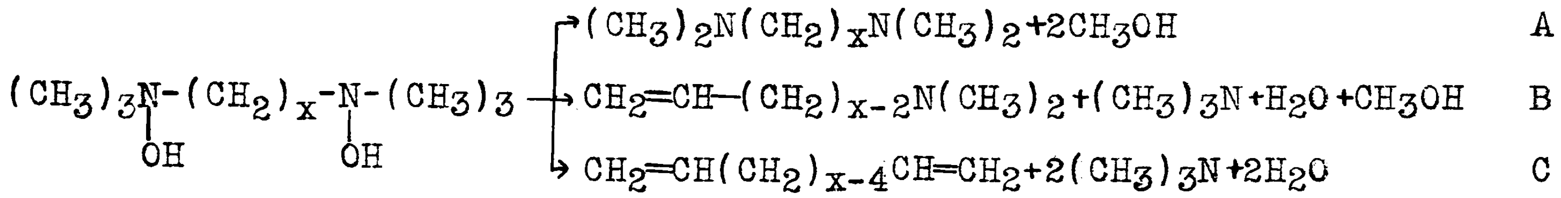
From the study of monoamines v. Braun (34) went on to diammonium compounds of the type:

$HO(CH_3)_3N(CH_2)_xN(CH_3)_3OH$

where X = 3, 5, 7 and 10

The decomposition of these compounds could yield besides the expected trimethylamine, water and methyl alcohol, a ditertiary amine (t-amine-R-t,-amine of the table below) an unsaturated tertiary amine (olefin-R-t.-amine) or a di-olefin (olefin-R-olefin), depending on which of three possible courses the decomposition followed; as seen from the table, all three possibilities were encountered,

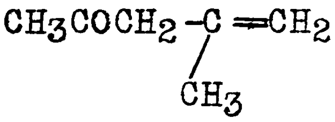
(35b) Ishzaka, N. Ber. 47 2456-60 (1914).



$$(CH_3)_3\underset{OH}{N}-(CH_2)_x-\underset{OH}{N}-(CH_3)_3 \rightarrow \begin{cases} (CH_3)_2N(CH_2)_xN(CH_3)_2+2CH_3OH & A \\ CH_2{=}CH-(CH_2)_{x-2}N(CH_3)_2+(CH_3)_3N+H_2O+CH_3OH & B \\ CH_2{=}CH(CH_2)_{x-4}CH{=}CH_2+2(CH_3)_3N+2H_2O & C \end{cases}$$

	<u>A</u>	<u>B</u>	<u>C</u>
diammonium base	t.amine-R-t.-amine obtained in %	olefin-R-t.amine obtained in %	olefin-R-olefin obtained in %
$(CH_3)_3\underset{OH}{N}(CH_2)_{10}\underset{OH}{N}(CH_3)_3$	50	30	20
$-(CH_2)_7-$	50	30	15
$-(CH_2)_5-$	negligible	negligible	about 100
$-(CH_2)_4-$	"	"	" "
$(CH_2)_3-$	"	"	" "

The diolefin produced in the C_{10} compound was not examined but it was presumably the decadiene-1,9; the reaction when $X = 4$ yielded butadiene and the process was made the subject of a patent (36). In the C_3 series, the expected diolefin was allene, $CH_2{=}C{=}CH_2$, but this was not obtained; instead there appeared an unsaturated ketone $C_6H_{10}O$, which might have arisen from the addition of water to the fragment $\left[\dot{C}H_2-\underset{\wedge}{C}-\dot{C}H_2\right]$, and for which the structure

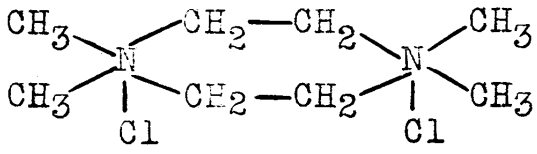


$$CH_3COCH_2-\underset{CH_3}{C}{=}CH_2$$

was suggested. K norr and Roth (37) had observed the occurrence of what seemed to be this same ketone, when on heating the methylated piperazine dichloride

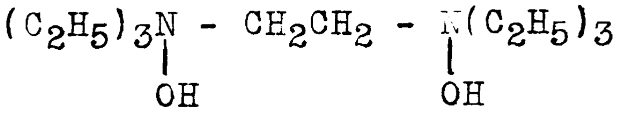
(36) F.Bayer & Co.,Brit.8100 (1910) "Synthetic Rubber" D.Van Nostrand Co., (1926) p.44.

(37) Knorr, L., Roth, P., Ber. <u>39</u> 1420-29 (1906).



with strong potassium hydroxide solution, it was evolved along with allyldimethylamine and tetramethyltrimethylenediamine.

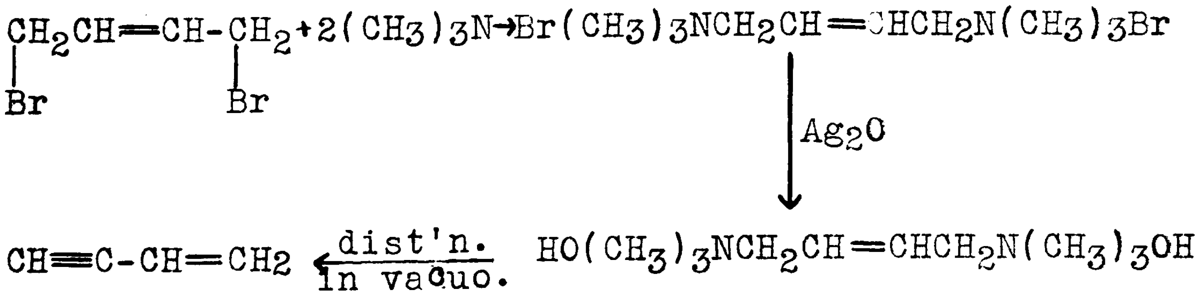
The behaviour of the first member of the diammonium series - that is, hexamethylethylenediammonium hydroxide does not appear to have been investigated, but Solonina (29) showed that one of the decomposition products from hexaethylethylenediammonium hydroxide



$$(C_2H_5)_3\underset{OH}{N} - CH_2CH_2 - \underset{OH}{N}(C_2H_5)_3$$

was acetaldehyde, together with a little diethylamine.

A diammonium hydroxide already possessing an ethylenic link can be transformed on heating into an acetylenic compound. Thus, Willstätter and Wirth (38), and later Shilov and Maskashima (39) prepared vinylacetylene starting with: 4 dibromobutene-2.



$$\underset{Br}{CH_2}CH{=}CH{-}\underset{Br}{CH_2} + 2(CH_3)_3N \rightarrow Br(CH_3)_3NCH_2CH{=}CHCH_2N(CH_3)_3Br \xrightarrow{Ag_2O} HO(CH_3)_3NCH_2CH{=}CHCH_2N(CH_3)_3OH$$

$$CH{\equiv}C{-}CH{=}CH_2 \xleftarrow[\text{in vacuo.}]{\text{dist'n.}} HO(CH_3)_3NCH_2CH{=}CHCH_2N(CH_3)_3OH$$

(38) Willstätter, R., Wirth, T. Ber. 46 535-538 (1913).

(39) Shilov, E.A., Maskashima, A.M. Sinteticheskii,Kauchuk 1933 No.1, 4-12 Chem. Abs. 27 5052 (1933).

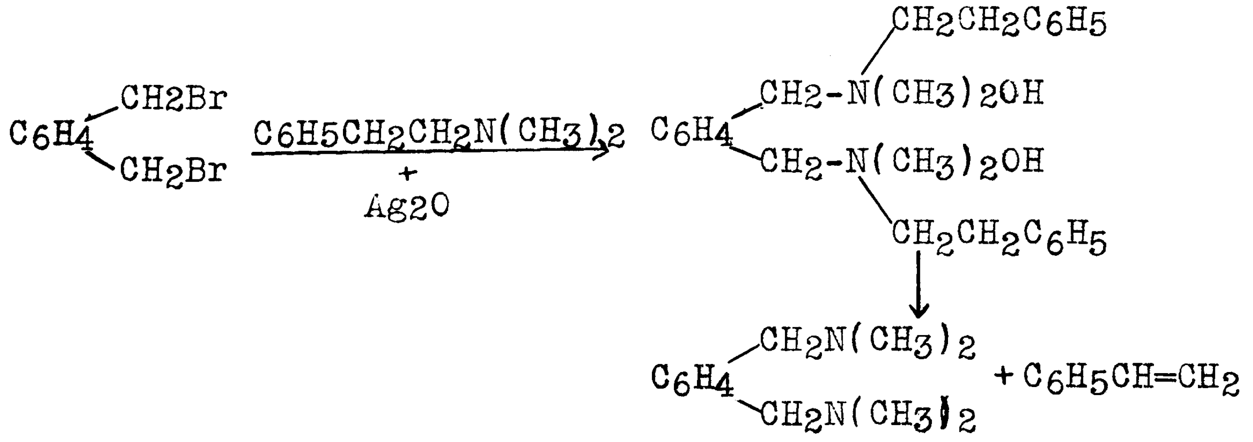
From v.Braun's results with the diammonium hydroxides it will be seen that the compounds studied yielded an unsaturated tertiary amine, the amount of which increased as X increased. The lower members of the series decomposed simultaneously at both ends of the chain, while the higher members changed first at one end only. Thus we have first,

$$HON(CH_3)_3(CH_2)_{10}N(CH_3)_3OH - \left[\begin{array}{l} \rightarrow H_2O + (CH_3)_3N + HO.N(CH_3)_3(CH_2)_8CH{=}CH_2 \\ \\ \rightarrow CH_3OH + HO.N(CH_3)_3(CH_2)_{10}N(CH_3)_2 \end{array}\right.$$

and then

$$HO.N(CH_3)_3(CH_2)_{10}N(CH_3)_2 - \left[\begin{array}{l} \rightarrow H_2O + (CH_3)_3N + CH_2{=}CH(CH_2)_8CH{=}CH_2 \\ \\ \rightarrow CH_3OH + (CH_3)_2N(CH_2)_{10}N(CH_3)_2 \end{array}\right.$$

Another interesting diammonium hydroxide investigated by v.Braun (40) was that from o-xylylene bromide, and whose reactions are indicated in the following equations.

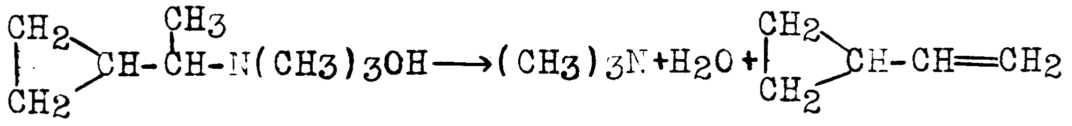


The styrene was recovered in 65% of the theoretical yield.

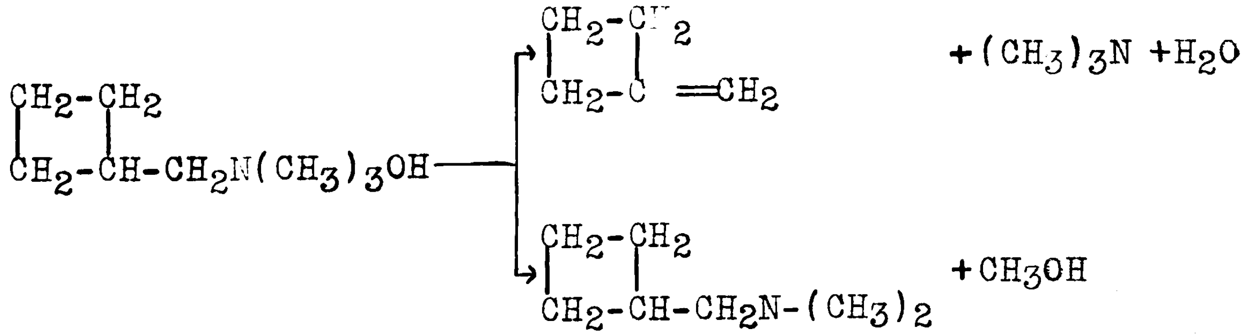
(40) v.Braun, J., Cahn, R.S. Ann. <u>436</u> 262-73 (1924).

Alicyclic-substituted Quaternary Ammonium Hydroxides.

The decomposition of quaternary ammonium hydroxides with alicyclic substituted alkyl groups has proven to be of synthetic value in preparing certain cyclopropane and cyclobutane derivatives. This was shown to be the case with methylcyclopropylmethyltrimethyl-ammonium hydroxide (41), which gave trimethylamine and cyclopropyl ethylene in over 70% yields, with only a little of the mixed tertiary amine,



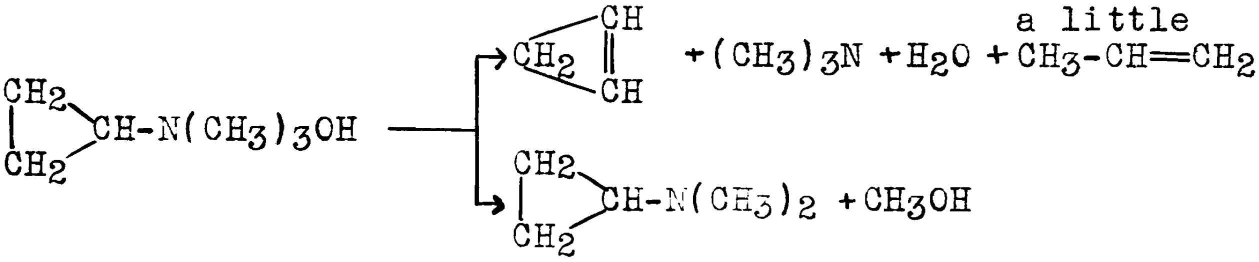
Cyclobutylmethyl-trimethyl ammonium hydroxide (42) decomposed in a similar manner to the foregoing example, but gave rather less hydrocarbon, and hence more of the mixed t.-amine and methyl alcohol (32%).



Demjanov and Dojarenko, continuing their investigations with the same type of compound found that from cyclopropyltrimethylammonium hydroxide (43) there was formed a still smaller

(41) Demjanov, N.J., Dojarenko, M. Ber. 55B 2718-27 (1922).
(42) Demjanov, N.J., Dojarenko, M. ibid 2727-30 (1922).
(43) Demjanov, N.J., Dojarenko, M. Ber. 56B 2200-07 (1923).

proportion of unsaturated hydrocarbon (60%) and about 40% of methyl alcohol and mixed tertiary amine. The decomposition was carried out at 300°, with the result that some of the cyclopropene obtained was found to have been changed to allene.



Later, they studied the effect of heat on the yields of cyclopropene (44) in this reaction, and found that at higher temperature (actual value not recorded) the yield of cyclopropene decreased while the allene increased. The proportion was about 37% of the former to 13% of the latter; at lower temperature, the ratio was 43% cyclopropene to 2% allene. Cyclopropylmethyltrimethyl ammonium hydroxide (45), in contrast to cyclobutylmethyltrimethylammonium hydroxide gave over 90% methyl alcohol and mixed tertiary amine; the 6.5% of hydrocarbons obtained under optimum conditions of rapid decomposition of the hydroxide, was found to consist mostly of butadiene.

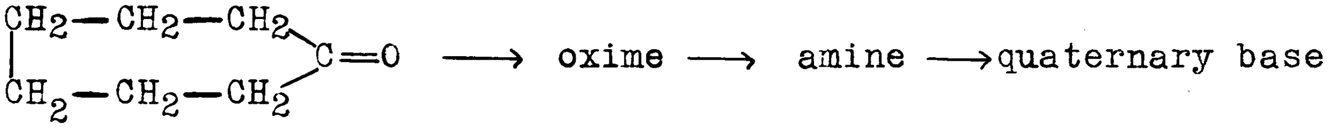
The earlier work on alicyclic substituted quaternary ammonium hydroxides was carried out by Willstätter and coworkers, in their classic researches on the structure and

(44) Demjanov, N.J.,Dojarenko, M.,Bull. Acad. sci. union rép. soviet social, classe sci. phys. math. (1929) no.7 653-65 Chem. Abs. 24 1848 (1930).

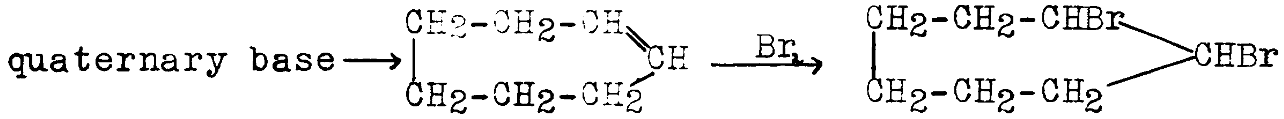
(45) Demjanov, N.J., Dojarenko, M. Ber.56B 2208-12 (1923).

synthesis of tropidine, tropine and relative substances and in the chemistry of other alicyclic compounds.

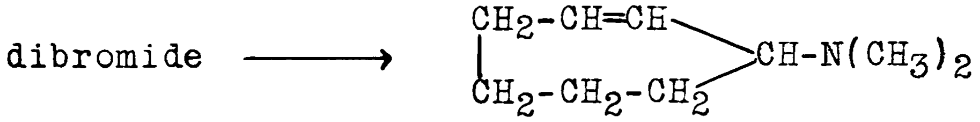
The synthesis of tropilidene (46) was accomplished in the following manner. Suberone was converted to its oxime



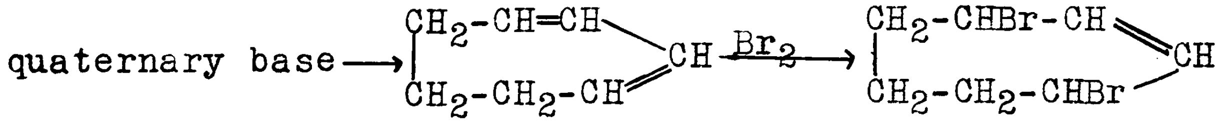
this reduced to the amine and the quaternary ammonium hydroxide distilled with the production of cycloheptene.



The dibromide of this, on treatment with dimethylamine in benzene gave dimethylamino Δ^2- cycloheptene in excellent yields.



When cycloheptenetrimethylammonium hydroxide, made in the usual manner by the addition of methyl iodide to the tertiary amine followed by treatment with moist silver oxide, was distilled, cycloheptadiene or hydrotropilidene was produced.



cycloheptadiene

Cycloheptene dibromide was obtained by the addition of bromine to the conjugated system in cycloheptadine and by treatment

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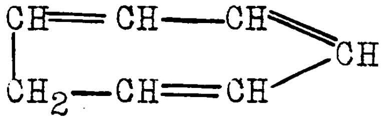
(46) Willstätter,R., Ann. 317 204-265 (1901)

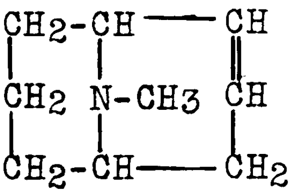
with dimethylamine and exhaustive methylation of the resulting tetramethyldiaminocycloheptene, gave,

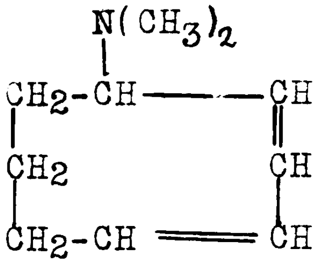
cycloheptatriene
or tropilidene
in almost quant. yields



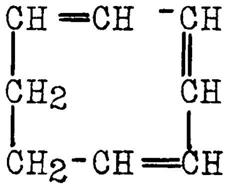
Using the same technique of first producing a quaternary ammonium hydroxide, decomposing to an unsaturated cyclic compound, brominating to obtain an unsaturated dibromide, treatment with dimethylamine, and further exhaustive methylation, Willstätter and co-workers in a series of papers (47) extending over eight years, accomplished the synthesis of cyclooctatetraene, and all the intermediate unsaturated compounds of the cyclooctane series.

N-methyl granatenine was converted to,





α-des-dimethylgranateine

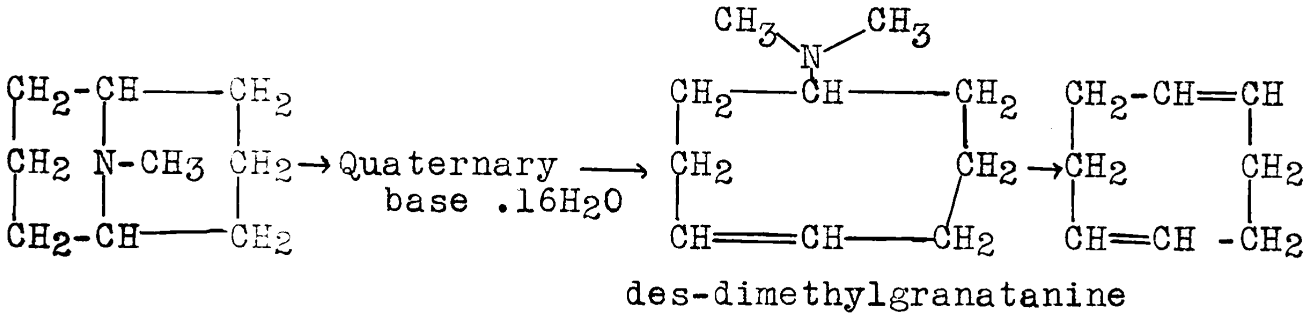


cyclooctatriene

the quaternary base and this on distillation at 10 mms. pressure and at a bath temperature of 100-110° produced α-des dimethylgranatenine in 90% yield. This new monocyclic base was converted to the quaternary hydroxide and again by vacuum distillation at 100-115° there was obtained trimethylamine, water and cyclooctatriene.

(47) Willstätter, R., Veraguth, H. Ber. 38 1975-84 (1905).
Willstätter, R., Waser, E. Ber. 44 3423-45 (1911).
Willstätter, R., Heidelberger, M. Ber. 46 517-527 (1913).

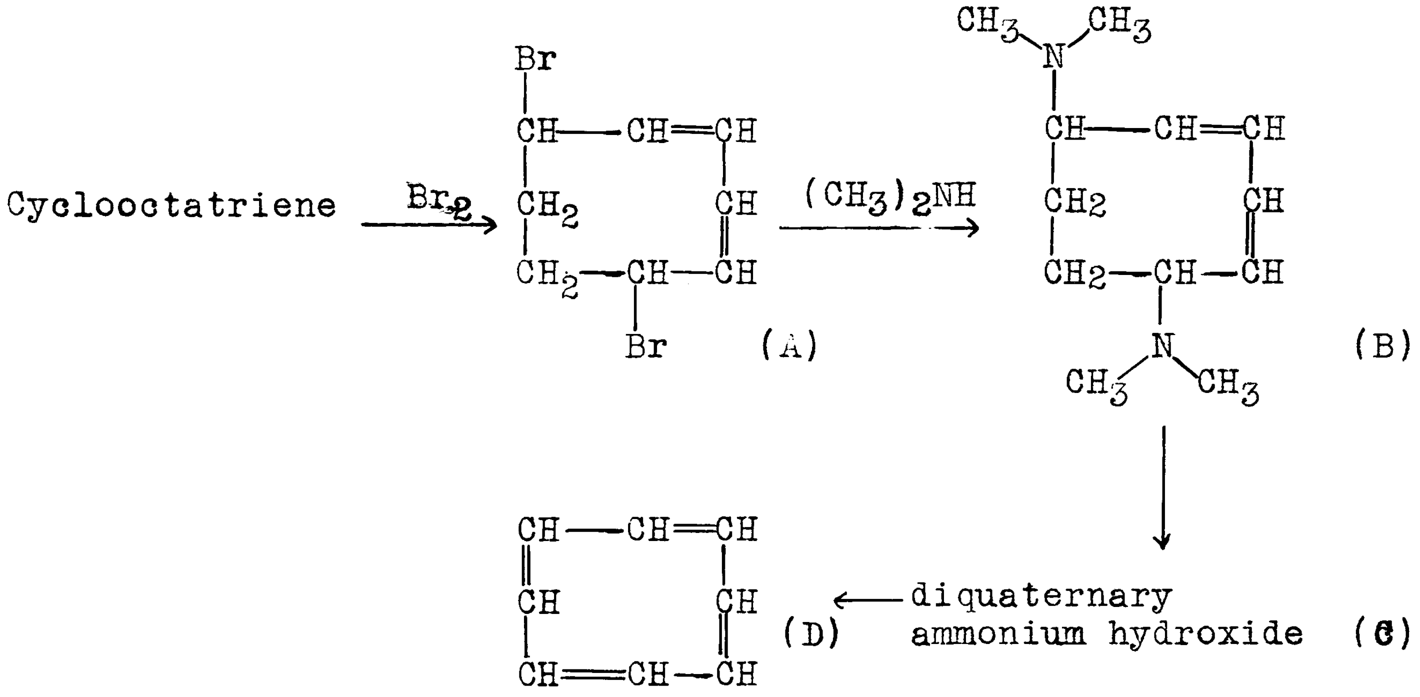
Cyclooctadiene (48) was produced by the same series of reactions, but starting with, N-methylgranatanine -



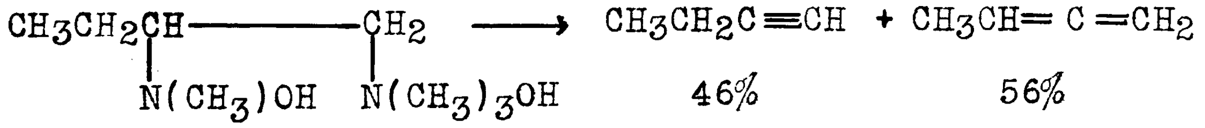
Catalylic reduction of the unsaturated tertiary amine before the exhaustive methylation, resulted in the formation of cyclooctene (49) itself.

Bromination of cyclooctatriene gave dibromcyclooctadiene, and this with dimethylamine yielded tetramethyldiaminocyclooctadiene. By exhaustive methylation of this amine, Willstätter and Waser obtained cyclooctatetraene in about 40% yield. The decomposition, when carried out in the vacuum of an oil pump, proceeded at 85-90°; with a water-pump vacuum, the temperature had to be increased to 110° and then the hydrocarbon produced was contaminated with a dicylic impurity.

(48) Willstätter, R., Veraguth, H. Ber. 38 1984-91 (1905).
(49) Willstätter, R., Waser,E. Ber. 43 1176-83 (1910).



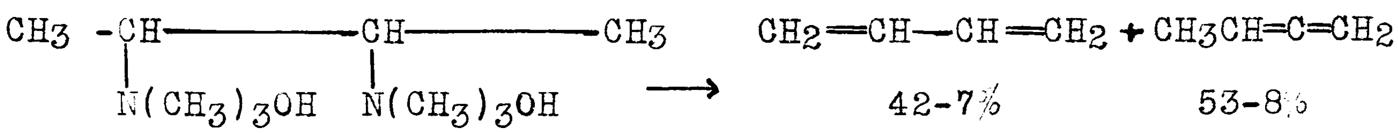
It will be observed that Willstätter had assumed the formation of conjugate double bonds in all cases of exhaustive methylation. Hurd and Drake (50) have recently shown that this assumption appeared to be unjustified. They prepared 1,2 butane bis(trimethylammonium) bromide, which on conversion to the hydroxide and subsequent pyrolysis at 200-250° gave 46% of ethylacetylene, and 56% of methylallene, but no 1,3 butadiene.



$$\underset{N(CH_3)OH}{CH_3CH_2CH}\text{———}\underset{N(CH_3)_3OH}{CH_2} \longrightarrow \underset{46\%}{CH_3CH_2C\equiv CH} + \underset{56\%}{CH_3CH{=}C{=}CH_2}$$

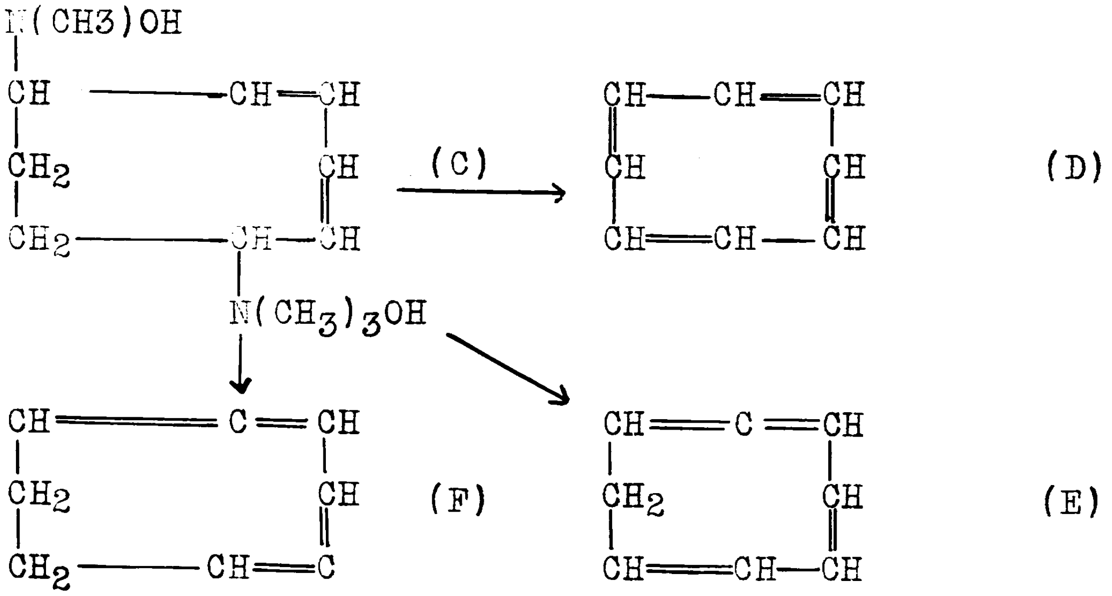
The bis hydroxide formed in the same manner from 2,3 dibromobutane, gave 42-7% of 1,3 butadiene and 53-8% of methylallene (or methylallene + dimethylacetylene).

(50) Hurd, C.D., Drake, L.R. J. Amer. Chem. Soc. <u>61</u> 1943-5 (1939).



$$CH_3-\underset{N(CH_3)_3OH}{\underset{|}{CH}}-\underset{N(CH_3)_3OH}{\underset{|}{CH}}-CH_3 \longrightarrow \underset{42\text{-}7\%}{CH_2=CH-CH=CH_2} + \underset{53\text{-}8\%}{CH_3CH=C=CH_2}$$

From the fact that no 1,3 butadiene was obtained in the pyrolysis of the 1,2 substituted butane bis-ammonium hydroxide (a product not normally to be expected, but which might have occurred through rearrangement at the temperature of the experiment, of ethylacetylene); and since the 2,3 substituted butane bis-ammonium hydroxide did not yield exclusively 2,3 butadiene, these authors questioned the validity of Willstätter's assumption that conjugated systems were always formed. They went on to show that by considering the formation of every possible isomer from the two Hofmann degradations, from the bromination of the resulting triene, and the conversion of the dibromo-diene to the bis quaternary ammonium hydroxide, and assuming no molecular rearrangements en route, that there was the possibility of the occurrence of from 1 to 14 isomeric bis-quaternary hydroxides. Of these, only the one assummed by Willstätter and Waser would give the conjugated tetraene on the last pyrolysis if shifting of double bonds be still ruled out; and in addition to the conjugated tetraene there might also occur the 2 other isomers as shown:



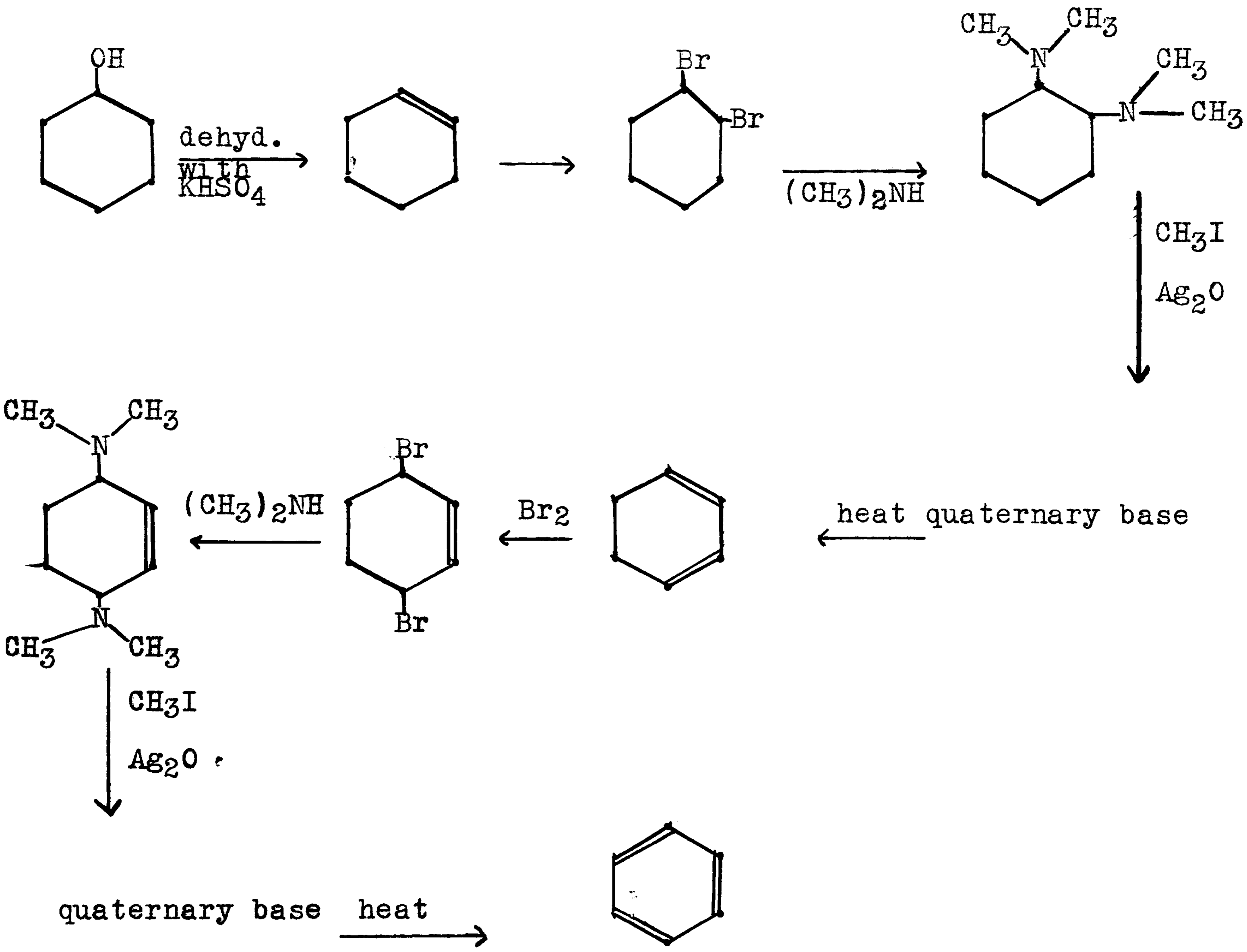
Willstätter himself, by showing that the amine(compound B page 34) derived from the dibromodiene (A) with dimethylamine was not homogeneous but contained a small amount of a readily hydrolysable amine, (such as would be formed from a non-conjugated dibromide) tacitly admitted that the ethylenic bonds formed on pyrolysis of quaternary ammonium hydroxides were not exclusively in the conjugated position. But as to the constitution of the final product, in view of the general tendency for double bonds in chain systems longer than the butane series to rearrange to the conjugated state, and particularly when as in this case by doing so they reach a condition of complete conjugation, it seems rather unlikely that Willstätter's cyclooctatriene has not the structure (D) he assigned to it.

Additional support for Willstätter's view that cyclooctatetraene was really synthesized lies in the fact that on hydrogenation, a substance m.p.6^{o} was obtained and which must have been impure cyclooctane since on oxidation it yielded suberic acid. Recent critics of Willstätter's work have suggested that the tetraene was actually styrene; there has, however, been no definite evidence yet produced to disprove Willstätter's contentions.

In the cyclobutane series, Willstätter (51) found, as was to be expected, that cyclobutylamine on exhaustive methylation, decomposed in both possible directions, to give cyclobutene, water and trimethyl amine and also cyclobutyldimethyl amine and methyl alcohol. The cyclobutene obtained was found to be contaminated with butadiene in amounts up to 10%.

In a manner somewhat similar to that used in the synthesis of cyclooctatetraene Willstätter (52) converted cyclohexanol to benzene. The various steps in the synthesis are indicated as follows:

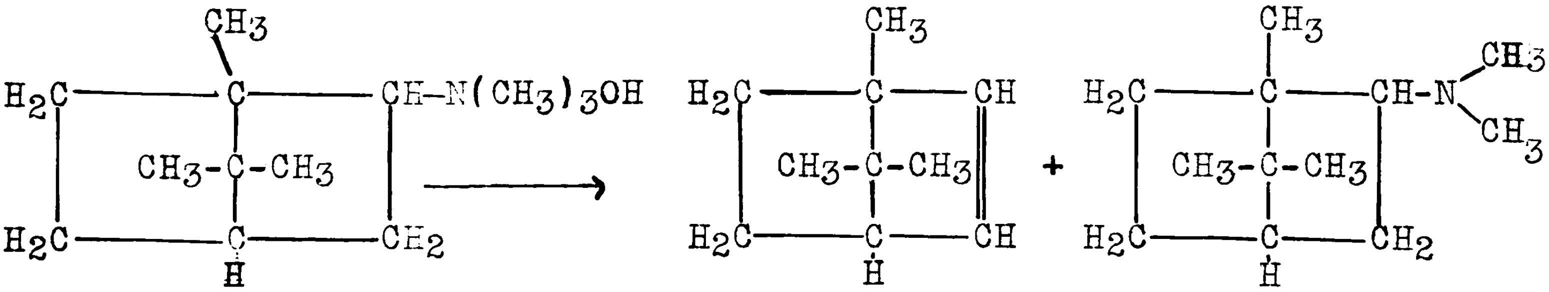
(51) Willstätter, R., v.Schmaedel, W. Ber.38 1992-99 (1905).
Willstätter, R., Bruce, J. Ber. 40 3979-99 (1907).
(52) Willstätter, R., Hatt, D. Ber. 45 1464-71 (1912).



Quaternary Ammonium Hydroxides of the Terpene Series.

The decomposition of quaternary ammonium bases has been a most useful tool in solving some of the problems of terpene chemistry, particularly since the unsaturated compounds so produced have not undergone rearrangement except where the hydrocarbon would be expected to rearrange as a result of the temperatures used in carrying out the decomposition.

Wallach (53) for example prepared both cis and trans menthyltrimethylammonium hydroxide in the usual manner from menthyl amine, and by distillation of the free base at atmospheric pressure (temperature not given) obtained trimethyl amine, water and menthene. Similarily Ruzicka (54) from d-bornyltrimethylammonium hydroxide distilled at 200° at a pressure of 0.125 mms., obtained l-bornylene and bornyldimethylamine in the ratio of 2:1.



$+H_2O + (CH_3)_3N + CH_3OH$

This was not, however, as Ruzicka supposed the first instance of the transferance of this method of preparation from the alkaloids to the terpenes. Shriner and Sutherland (55) have recently shown that the maximum purity of bornylene obtainable by this method is 96%, the chief impurity being the isomeric d-camphene. The specific rotation of Shriner's bornylene was -18.1°, whilst the highest recorded rotation, -23.94°, reported by Bredt (56) for a sample prepared from β-iodohydrobornylene-carboxylic acid.

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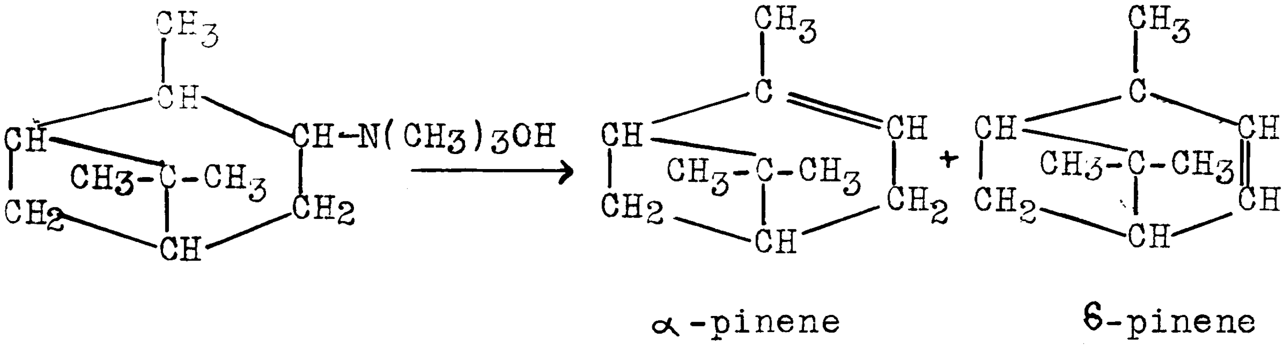
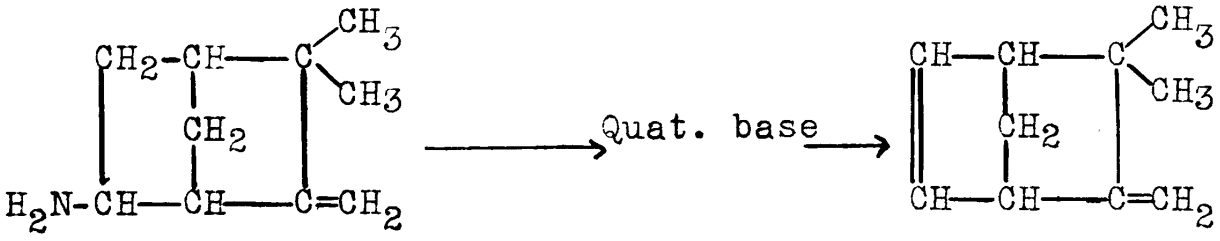
(53) Wallach, O. Ann. 300 278-285 (1898).
(54) Ruzicka, L., Rotheim, E. Helv. Chim. Acta. 3 748-52 (1920).
(55) Shriner, R.L., Sutherland, H. J.Amer. Chem. Soc.c60 1314-20 (1938).
(56) Bredt, J., Helbing, W. J. pr. Chem. (ii) 84 778-786(1911).

In the pinene series, Ruzicka (57) prepared α-pinene by the distillation of pinocamphyltrimethylammonium hydroxide at 150°- 200° and 0.7 mms. pressure.



Another rather difficultly obtainable terpene hydrocarbon was isocamphodiene, which was prepared (58) by cautious distillation of the quaternary base from α-aminocamphene,



α-amino camphene

In the cases thus far considered, it will be seen that in the production of a hydrocarbon by distillation of a quaternary ammonium hydroxide, hydrogen is removed from a

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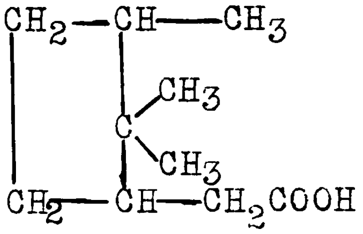
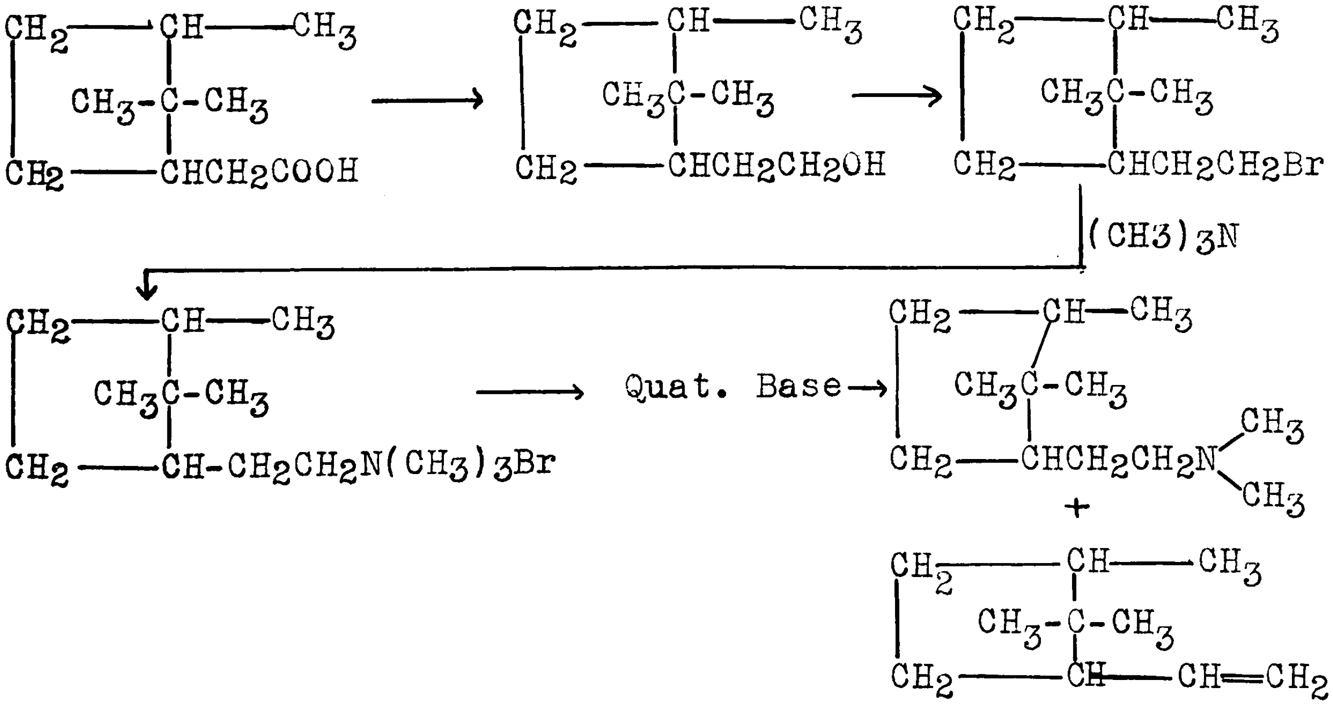
(57) Ruzicka, L., Trebler, H. Helv. Chim. Acta 3 756-761 (1920).
(58) Nametkin, S.S. Zabrodin, A. Ber. 61B 1491-4 (1928).

carbon atom in the β-position to the nitrogen. v.Braun (59) has made use of this fact in demonstrating the presence of a CH_2 group adjacent to a carboxyl, and the particular compound he investigated was isocampholic acid -



Starting with the corresponding carbinol, he prepared the bromide, and this, on treatment with trimethylamine, gave the quaternary ammonium bromide. The salt, with silver oxide gave the base, which in turn on distillation in the presence of potassium hydroxide yielded mixed tertiary amine in 50% yield, and the unsaturated hydrocarbon in about 40% yield. The occurrence of this cyclic hydrocarbon with the unsaturated side chain was proof of the presence of a CH_2 adjacent to the carboxyl in the original acid.



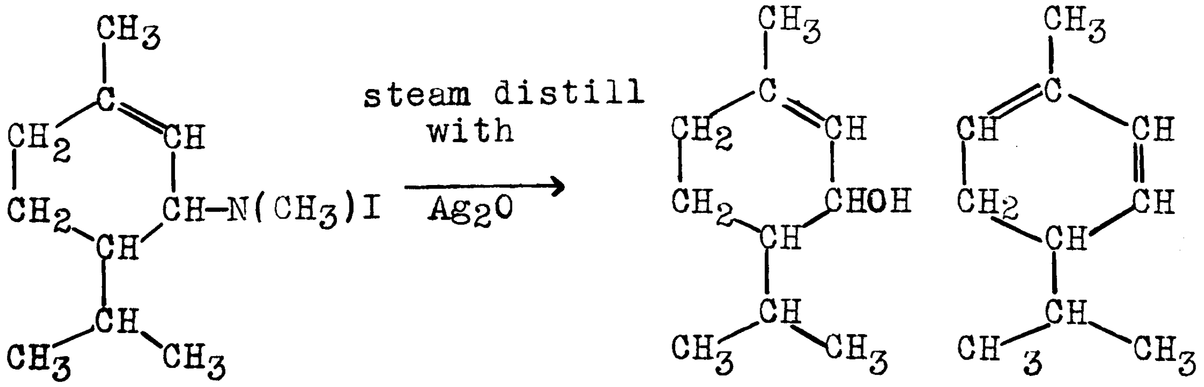
(59) v.Braun, J., Heymons, A. Ber. 61B 2276-80 (1928).

This same reaction can easily be adapted to the preparation of aldehydes and ketones, especially in cases where acids and alcohols of the type RCH_2COOH and RCH_2CH_2OH are readily available while the carbonyl compounds with one carbon atom less are not. v.Braun and co-workers (60) prepared the bromide from dihydrocitronellol, and from this, with trimethylamine and silver oxide, the quaternary hydroxide. Distillation gave the olefin ,

$$(CH_3)_2CH(CH_2)_3CH(CH_3)CH{=}CH_2$$

which on ozonolysis produced the isononaldehyde. Similarly . from ethyloctyl acetic acid, via β-ethyl - β-octylethyl alcohol, bromide and quaternary base, there was obtained an olefin, which on ozonolysis, gave ethyl octyl ketone.

Read and co-workers (61) have used the process of exhaustive methylation in their work on piperitone. When 1-piperityltrimethylammonium iodide was steam distilled in the presence of silver oxide and water, there was obtained, in addition to trimethyl amine, d-piperitol, and a terpene shown to be d α-phellandrene,



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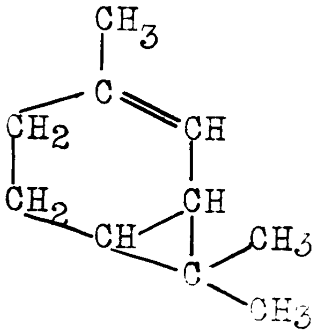
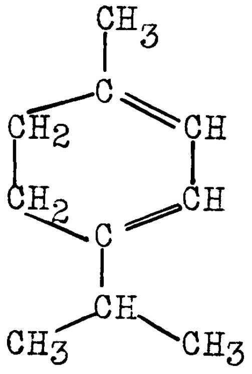
(60) v.Braun, J., Teuffert, W., Manz. G., Ber. 62 B. 235-41 (1929).
(61) Read, J., Storey, R.A., J. Chem. Soc. 1930 270-83.

Careful search failed to reveal the presence of either Δ^4 carene or α terpinene,

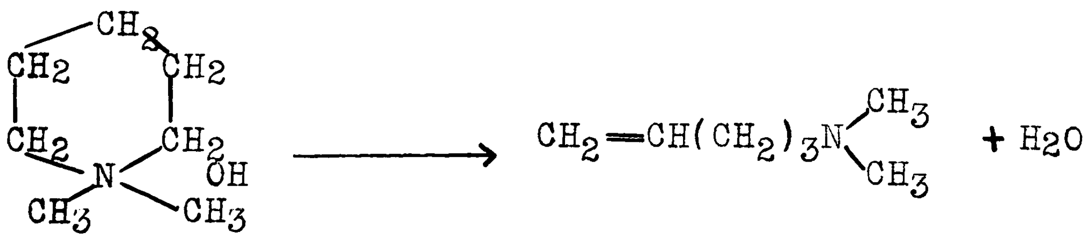




the expected terpenes.

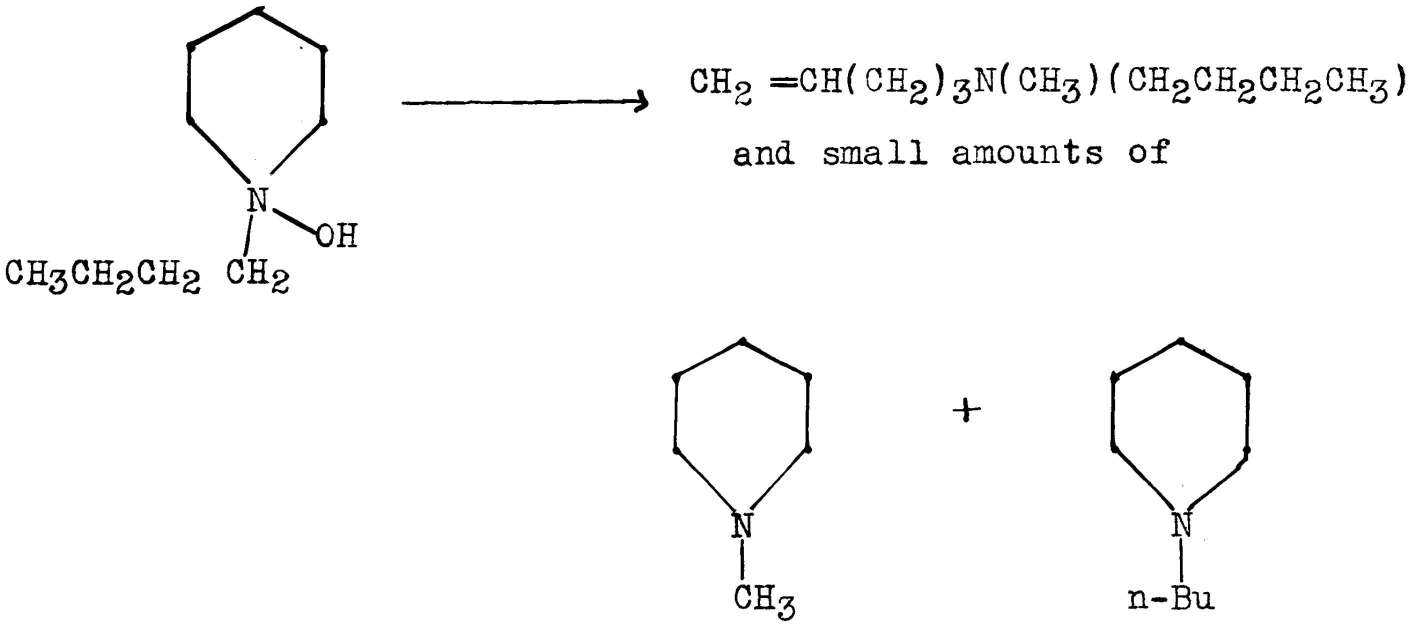
Quaternary Ammonium Hydroxides of Cyclic Amines.

It has already been pointed out that Hofmann, in the course of his work on amines, applied the process of exhaustive methylation to some cyclic amines, and found that on decomposition the ring had opened, with the formation of an unsaturated tertiary amine. Thus, dimethylpiperidinium hydroxide(30) gave dimethyl amino-pentene and water.



In the case, however, where there was a hydrogen in the β-position to the nitrogen and not part of the ring, then such a compound on distillation generally did not undergo ring opening. Methylethylpiperidinium hydroxide and methylpropylpiperidinium hydroxide (65) gave ethylene and propylene, respectively, and water & N-methylpiperidine. In the latter instance, in addition to the main products of the reaction, there also appeared some N-propylpiperidine, methyl alcohol and very small amounts of open chain compounds.

An irregularity appeared in the behaviour of the N-alkyl piperidine series however, when v Braun (65) observed that N-butyl-piperidine underwent ring cleavage to produce methyl-n-butyl-Δ^4-pentenylamine in 60% yield.



Thus a kind of periodicity seemed to exist, for the N-methyl derivative was completely ruptured, the N-ethyl was not, the

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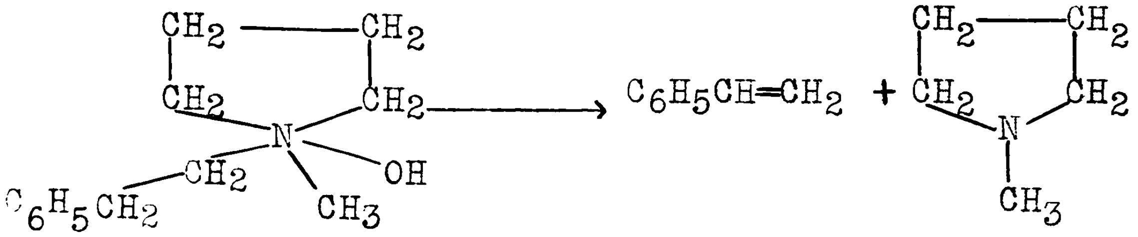
(65) v.Braun, J. Ber. 42 2532-8 (1909).

N-butyl very largely ruptured, and the isoamyl compound, which v.Braun also tried, was only partly cleaned.

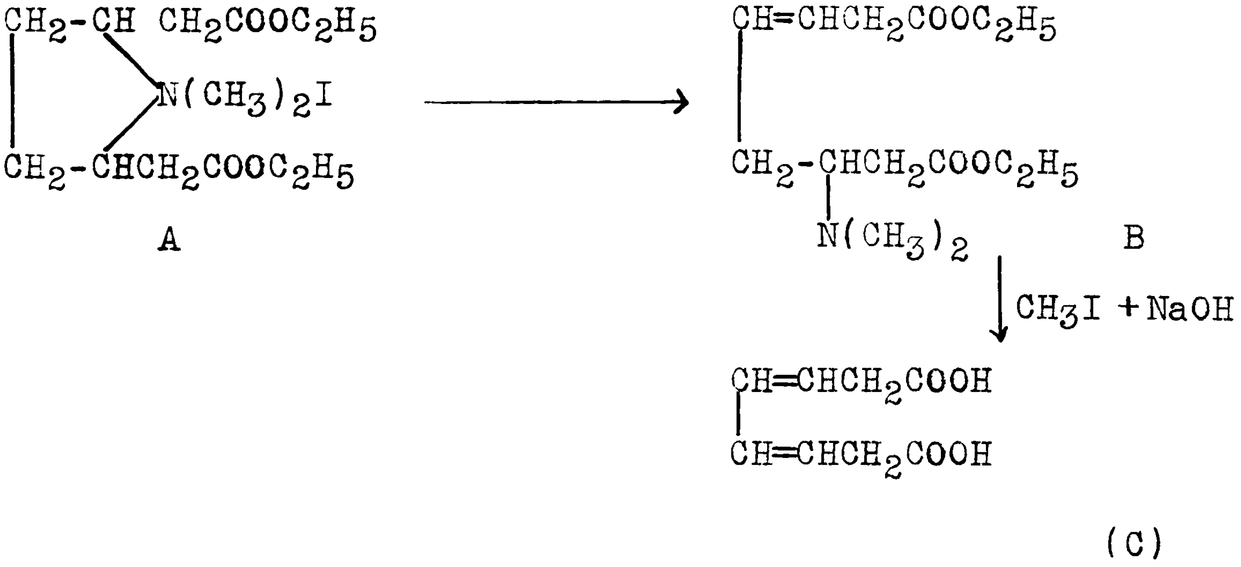
v.Braun and Buchman (65[a]) have recently repeated the decomposition of various N-methyl N-alkyl piperidine quaternary hydroxides, to find the effect of added potassium hydroxide and of glycerol on the relative amounts of product resulting from the different available directions of decomposition. In general it was observed that the production of an unsaturated compound, either by ring opening, or by the splitting off of the alkyl group as an olefin was favoured by the presence of potassium hydroxide. On the other hand, glycerol tended to lower the amount of decomposition in this direction, and to increase the production of methyl alcohol and an N-alkyl piperidine.

From pyrrolidine, in the same manner as from piperidine, there was obtained on exhaustive methylation, first dimethyl-Δ^3-propenylamine, and by further treatment of this with methyl iodide & silver oxide, butadiene. Following the analogy with the piperidine series, the N-substituted pyrrolidines did not undergo ring opening. v.Braun (40) found that from N-methyl N-phenylethylpyrrolidine hydroxide he obtained styrene in 60% of the theoretical yield, and no mention was made of any products resulting from rupture of the ring.

(65a) v.Braun, J., Buchman, E.R., Ber. 64B 2610-7 (1931)



When, however, the substituents were in the α,α' positions, the ring opened without difficulty and Willstätter (66) applied this reaction in the course of his synthesis of d,l-ecgonine and tropinone. He found that the pyrrolidine derivative (A), on treatment with concentrated potassium carbonate solution at 60°, decomposed with ring opening to give the unsaturated amino ester (B).



This was converted by a second treatment with methyl iodide and boiling sodium hydroxide, to trimethylamine and the unsaturated acid (C).

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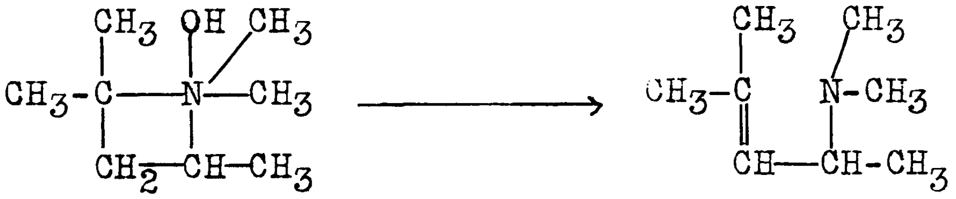
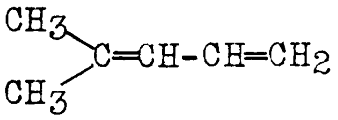
(66) Willstätter, R., Bommer, M. Ann. <u>422</u> 15-35 (1921).

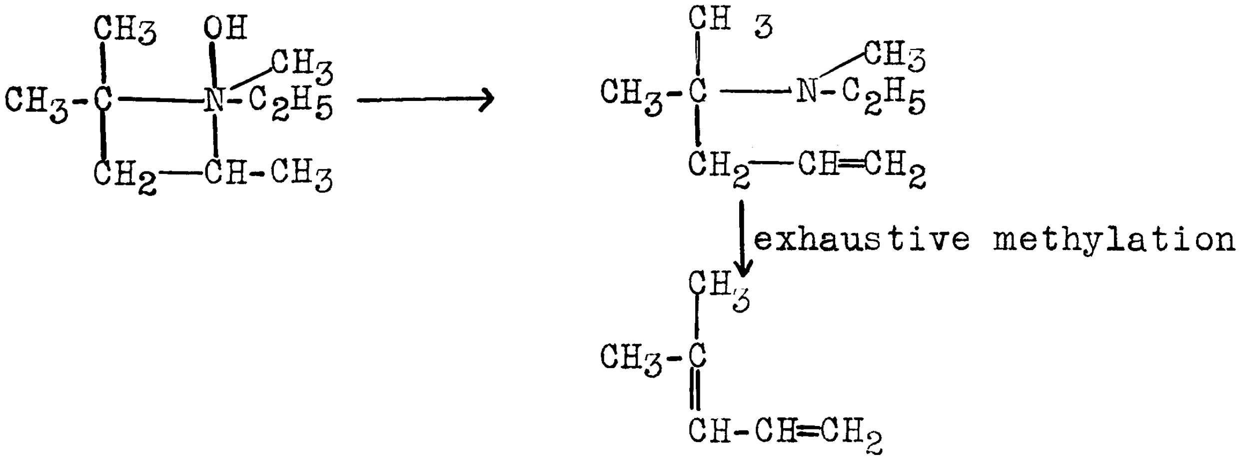
The investigations of Kohn and co-workers on four-membered ring compounds with nitrogen has been very interesting, but never seem to have been properly cleared up. Thus, they found that the quaternary base from 2,4,4-trimethyltrimethyleneimine (67)(68), underwent ring opening on heating in the manner shown.



The unsaturated amine so obtained on further treatment with methyl iodide, silver oxide, and distillation, gave the diene:

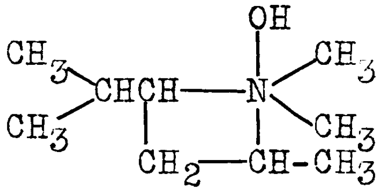


In the case of the quaternary base from 2,4,4 trimethyl-1-ethyltrimethyleneimine (69)(68) however, they found that the ring opened in a different position, to give an unsaturated tertiary amine, which on exhaustive methylation, gave the same diene as was obtained above.

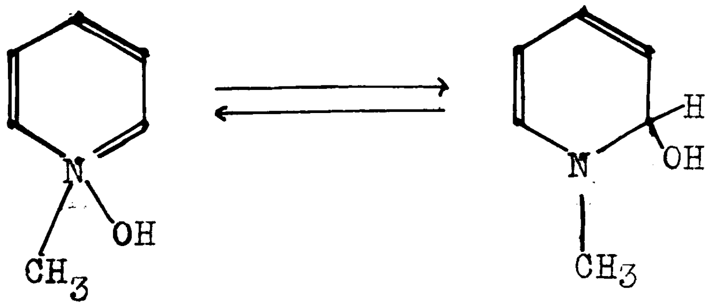


(67) Kohn, M. Ann. <u>351</u> 134-150 (1907).
(68) Kohn, M.,Morgenstern,O. Monatsh, <u>28</u> 529-536 (1907).
(69) Kohn, M.,Morgenstern,O. Monatsh, <u>28</u> 479-508 (1907).

A third compound studied by Kohn (70) in this series was the base from 1,2-dimethyl-4-isobutyltrimethyleneimine, but the products, resulting from its decomposition were not identified.



Pyridine, quinoline (71) and similar aromatic cyclic bases were found not to undergo ring opening on exhaustive methylation. Instead, the quaternary hydroxide underwent a reversible isomeric change in which the hydroxyl ion became covalently attached to the adjacent carbon atom, the valence of the nitrogen was reduced from five to three, and a shift of bonds in the ring rendered it no longer aromatic.



The isomers so produced are known as pseudo bases; (72) in the case of pyridine, the equilibrium is largely on the side of

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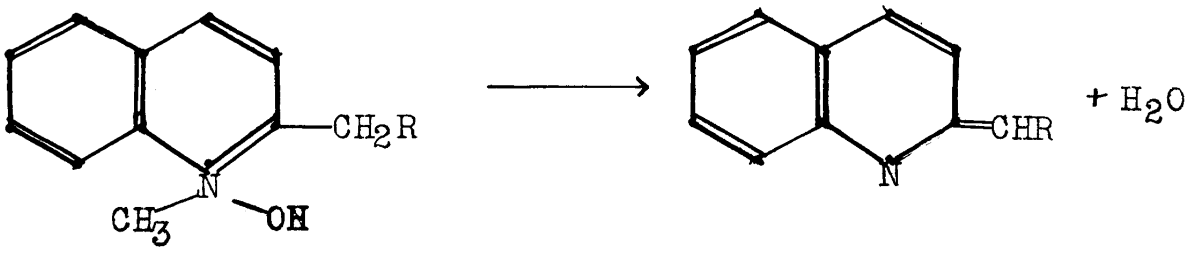
(70) Kohn, M., Giaconi J., Monatsh. 28 461-478 (1907).
(71) Decker, H., Kaufmann, A., J.prakt. Chem., 84 219-46 (1911).
(72) Sidgwick, N.V. Organic Chemistry of Nitrogen, Oxford University Press, 1937 p. 534-549.

the true base, but with quinoline, the reverse condition holds, in which the pseudo base is present in the higher concentration. The solution then exhibits the usual phenomena observed with all pseudo bases, of retarded neutralization, low electrical conductivity and the like.

The change from true base to pseudo base may be considered as a special case of quaternary ammonium hydroxide decomposition - analogous to the breakdown to tetramethylammonium hydroxide into a tertiary amine (the valence of nitrogen decreasing from 5 to 3) and an alcohol. The chief difference here is that the reaction is intramolecular and produces a compound that is both a tertiary amine and a carbinol.

Should the pyridine or quinoline base have an aliphatic substituent in the α or γ position (72), then there is the possibility of loss of water from the hydroxide to give an anhydro-base.



In the special case of 1,2 dimethylquinolinium hydroxide, Möller (73) has shown that methyl alcohol is split off leaving 2-methyl quinoline.

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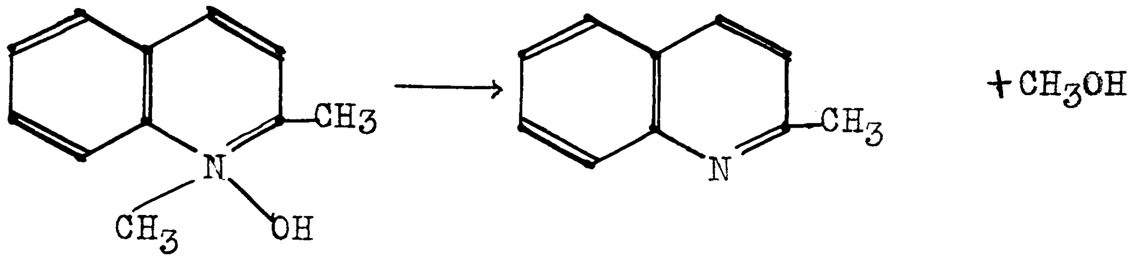
(73) Möller, M. Ann. 242 300-312 (1887).

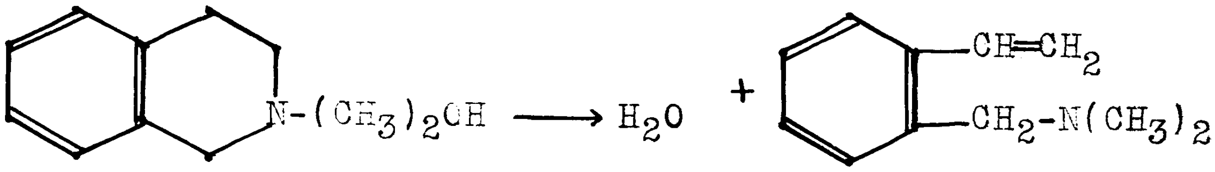


N-methylpyridyl hydroxide, on distillation with potassium hydroxide has been reported (74) to give N-methyldihydropyridine, but the amount was quite small.

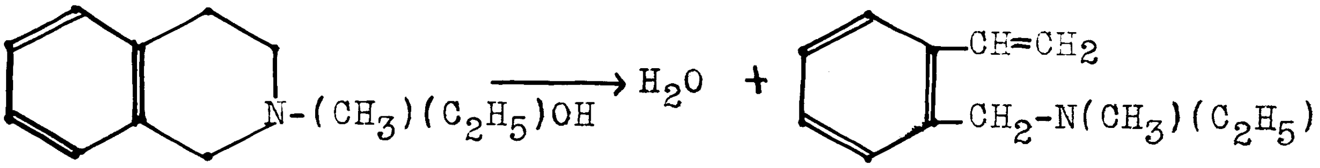
In contrast to the behaviour of N-alkyl piperidine derivatives on exhaustive methylation, the N-alkyl tetrahydroquinoline derivatives were not cleaved on heating the quaternary ammonium bases. Thus N-methyl (75)(65), N-ethyl (65) and N-propyl (65) tetrahydroquinoline on transformation to the corresponding quaternary bases, broke down again on heating to give varying amounts of either the original tertiary amine and methyl alcohol, or the N-methyl tetrahydroquinoline, an olefin and water.

Turning to the tetrahydroisoquinoline series, however, one again encounters ring opening on decomposition of the quaternary base. Thus, 2-methyltetrahydroisoquinoline on (76) exhaustive methylation, gave water and an unsaturated tertiary amine in 80% yield.

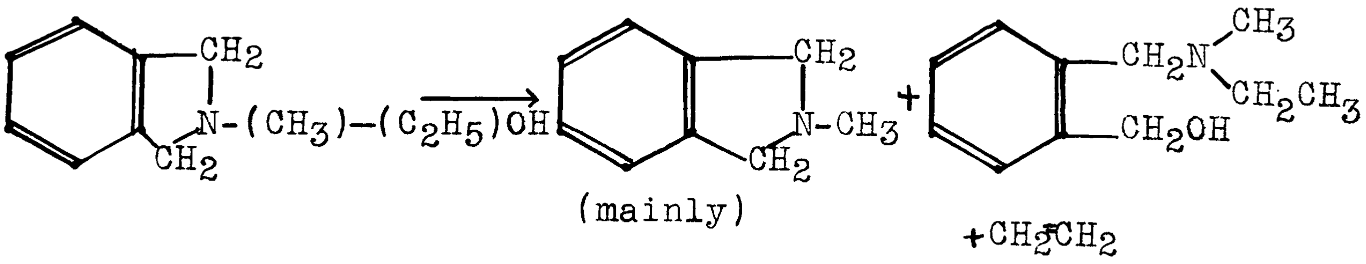
(74) Hofmann, A.W., Ber. 14 1498 (1881).
     Hofmann, A.W., Ber. 17 1908 (1884).
(75) Möller, M., Ann. 242-313-321 (320) (1887).
(76) Emde, H., Ann. 391 88-109 (100) (1912).



The homologous N-ethyl compound (77) decomposed in the same manner -



From the methylethyl quaternary base of dihydroisoindole, v.Braun obtained mainly ethylene and N-methyldihydroisoindole but there was also some of the o-hydroxymethyl compound resulting from a rupture of the carbon-to-nitrogen bond.

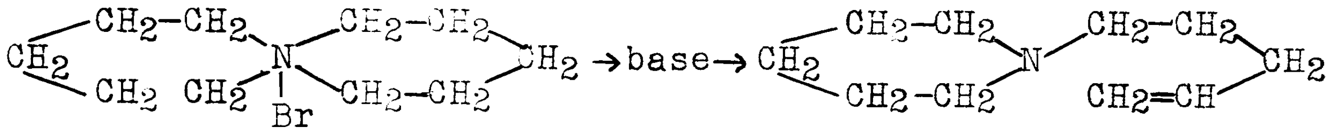


In the corresponding dimethyl base, more than half the reaction went to produce the o-hydroxymethyl tertiary amine.

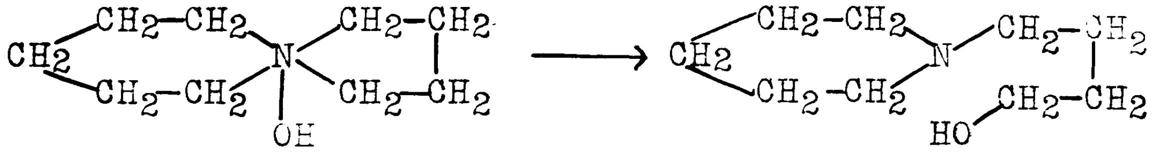
v.Braun and other workers have studied the relative stability of rings in cyclic bases under the condition of the Hofmann reaction. v.Braun (78) first observed that from the

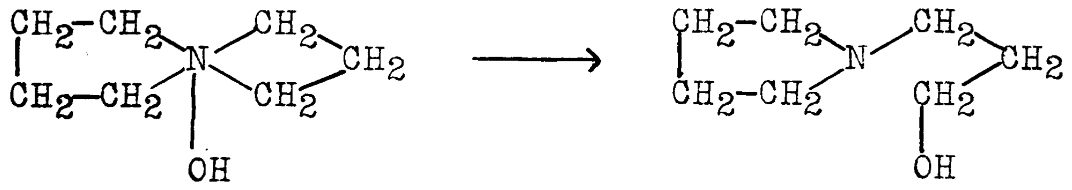
(77) v.Braun, J., Köhler, Z. Ber. 51 100-108 (1918).
(78) v.Braun, J., Müller, C., Beschke, E. Ber. 39 4347-57 (1906).

base of the bicyclic pentamethylenepiperidinium bromide he obtained the monocyclic, unsaturated base N-Δ^4-pentenyl-piperidine,



This was in contrast to the behaviour of tetramethylenepiperidinium hydroxide (79), and with trimethylenepyrrolidinium hydroxide (80), both of which decomposed with ring opening, but to produce the carbinol of the tertiary amine rather than the unsaturated tertiary amine.





The products from the decomposition of these two hydroxides indicate that the piperidine is more stable than the pyrrolidine ring, and this in turn, more stable than the four membered heterocyclic ring with nitrogen, under the condition of the Hofmann reaction.

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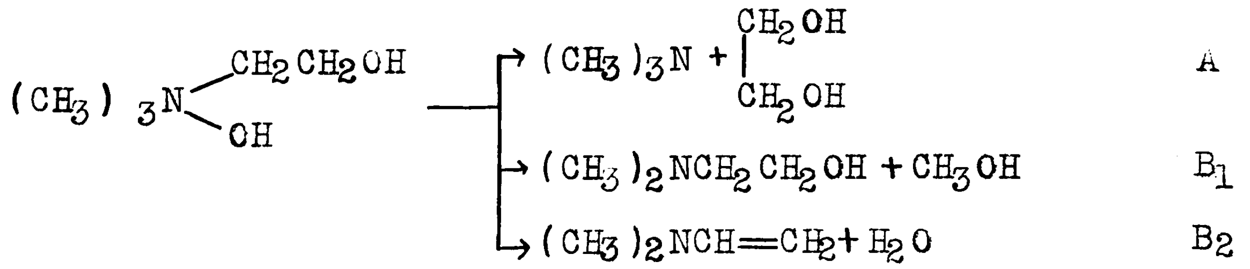
(79) v.Braun, J. Ber. 49 2629-42 (1916).
(80) Dunlop, J.G.M., J. Chem. Soc. <u>101</u> 1998-2003 (1912).

In much the same way, by synthesizing various compounds with the nitrogen common to two rings, and studying the nature of the decomposition products of the hydroxide, v.Braun (79)(81) tested the relative stability of a number of ring systems; his results indicate the following order of increasing ring stability: tetrahydroisoquinoline, moroph†oline, dihydroisoindole, pyrrolidine, piperidine, dihydroindole, tetrahydroquinoline, and homo-py-tetrahydroquinoline.

Cholines and related compounds.

The cholines and their derivatives, which are noteworthy in view of the fact that they are the only quaternary ammonium hydroxides occurring in nature, show some interesting reactions on decomposition.

Choline (82) itself decomposed in three ways, but the reaction was found to have proceeded chiefly according to equation A, below: only a very small amount of dimethylvinylamine was isolated.



$$\mathrm{(CH_3)_3N}\begin{cases}\mathrm{CH_2CH_2OH}\\ \mathrm{OH}\end{cases} \longrightarrow \begin{cases} \mathrm{(CH_3)_3N} + \begin{matrix}\mathrm{CH_2OH}\\ |\\ \mathrm{CH_2OH}\end{matrix} & \mathrm{A}\\ \mathrm{(CH_3)_2NCH_2CH_2OH + CH_3OH} & \mathrm{B_1}\\ \mathrm{(CH_3)_2NCH{=}CH_2 + H_2O} & \mathrm{B_2}\end{cases}$$

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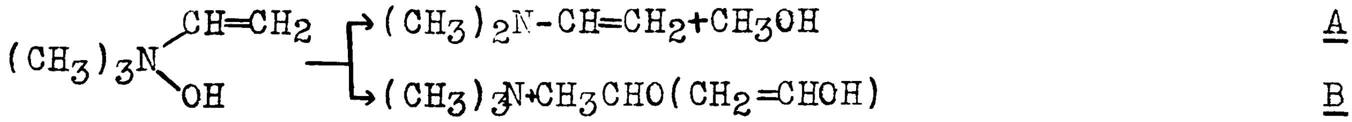
(81) v.Braun, J.,Köhler, Z. Ber. 51 255-265 (1918).
v.Braun, Seeman, J., Schultheiss, A., Ber. 55B 3803-17, 3817-25 (1923).
Horlein, H., Kneisel, R. Ber. 39 1429-35 (1906).
(82) Meyer, K.H., Hopff , H., Ber. 54 B. 2274-82 (1921).

Meyer and Hopff (82) obtained this tertiary vinyl amine in varying amounts from the decomposition of a number of other hydroxides; (β-diethylaminoethyl)-trimethylammonium hydroxide decomposed largely according to equation A, but there was also isolated, the products in equation B,

$$(C_2H_5)_2N\text{-}CH_2CH_2\text{-}N(CH_3)_3OH \begin{cases} \rightarrow (C_2H_5)_2N\text{-}CH_2CH_2\text{-}N(CH_3)_2 + CH_3OH & \underline{A} \\ \rightarrow (CH_3)_3N\text{-}H_2O + (C_2H_5)_2N\text{-}CH{=}CH_2 & \underline{B} \end{cases}$$

Neurine (82), on the other hand, followed chiefly the course indicated by equation B.



$$(CH_3)_3N\begin{matrix}\diagup CH{=}CH_2 \\ \diagdown OH\end{matrix} \begin{cases} \rightarrow (CH_3)_2N\text{-}CH{=}CH_2 + CH_3OH & \underline{A} \\ \rightarrow (CH_3)_3N + CH_3CHO(CH_2{=}CHOH) & \underline{B} \end{cases}$$

The neurine used in these experiments was isolated as the colourless, crystalline trihydrate, by concentration of a filtered solution of the base in a high vacuum over phosphorous pentoxide at 5-10°.

In the case of a substituted higher homologue of choline-allylhomocholine (83), v.Braun found that by treating the quaternary iodide with silver oxide, he obtained, not the free base but the amine oxide,

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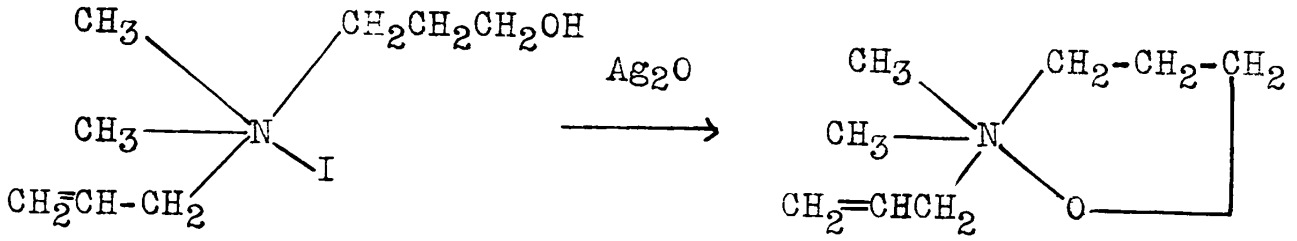
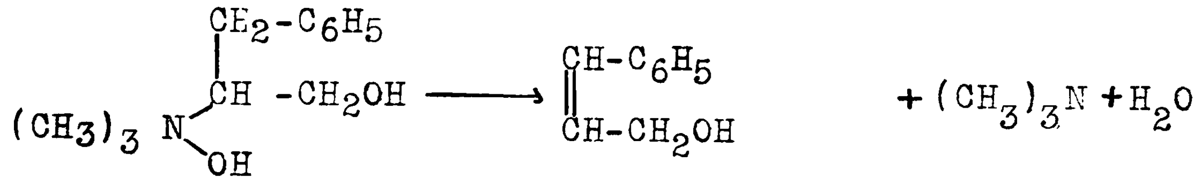
(83) v.Braun, J., Müller, E., Ber. 50 290-3 (1917).



Karrer and Horlacher (84) observed with phenylalamine choline, merely by shaking with silver oxide, that the decomposition proceeded exclusively to produce trimethylamine, but that instead of obtaining the glycol, as with choline, an unsaturated alcohol (cinnamyl) was formed.



The presence of a methoxy group in the para position in the benzene ring was apparently without influence on the course of the reaction. for here, p-methoxy cinnamyl alcohol was obtained.

A third possible reaction product besides an unsaturated alcohol, or glycol from the decomposition of a choline with evolution of trimethyl amine, is a substituted ethylene oxide, and these have frequently been observed to occur .

Thus the following isomers of phenylalanine choline (85) derived from ephedrine, pseudo ephedrine and isoephedrine

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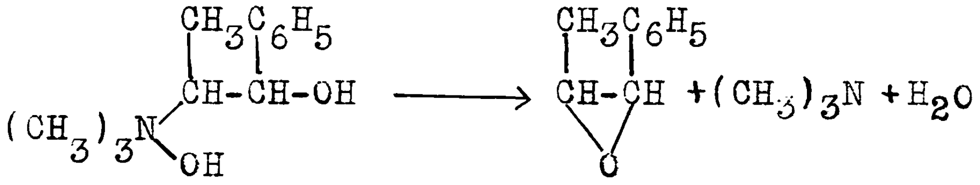
(84) Karrer, P., Horlacher, E., Helv. Chim. Acta <u>5</u> 571-5(1922).

(85) Emde, H., Runne, E. Ber. <u>43</u> 1727-9 (1910).
Rabe, P., Hallensleben, J., Ber. <u>43</u> 2622-3 (1910).
Schmidt, E., Arch. Pharm. <u>253</u> 52-6 (1915).

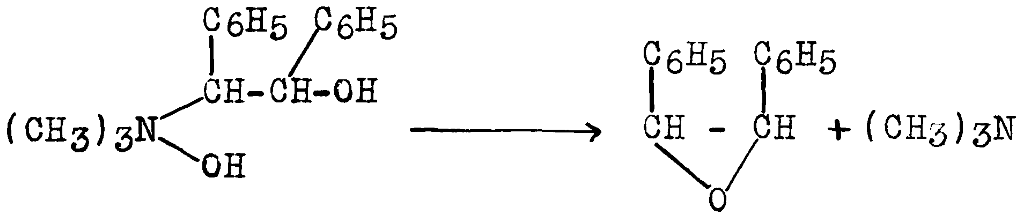
decomposed as shown,



(40%)

Besides these products however, a number of others have been obtained as well, including some of the glycol, ethyl phenyl ketone (the keto form of the unsaturated carbinol $C_6H_5\underset{OH}{C}{=}CHCH_3$), methyl ephedrine, ephedrine and a complex addition product of ephedrine with methylphenylethylene oxide.

From β-hydroxy-α, β-diphenylethylamine, Rabe and Hallensleben (86) obtained a quaternary iodide, which on treatment with moist silver oxide gave a solution of the base; on warming, trimethyl amine was evolved, and diphenylethylene oxide formed in 68% yield.



By starting with the isomeric diphenylhydroxyethyl amine, the isomeric diphenylethylene oxide was obtained in 62% yield.

Other substituted cholines (87) of the type

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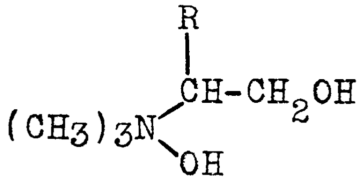
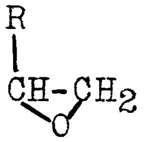
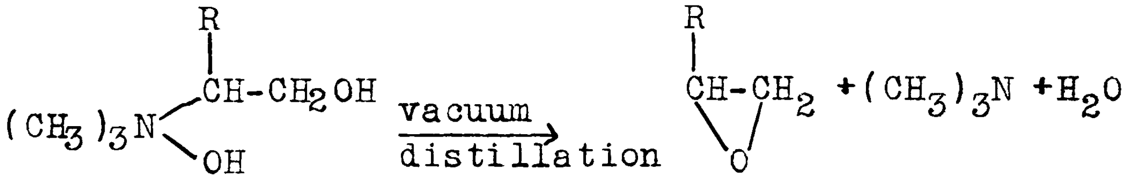
(86) Rabe, P., Hallensleben, J. Ber. 43 884-6 (1910).
(87) v.Braun, J., Schirmacher, W. Ber. 56B 1845-50 (1923).
v.Braun, J., Ber. 56B 2178-85 (1923).

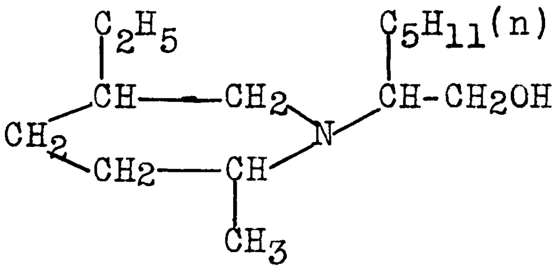


which on decomposition gave only the ethylene oxide  and no glycol, are included in the following table, which shows the nature of R and the yield of oxide obtained.



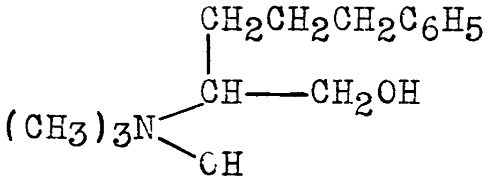
R	yield of oxide in %
$CH_3CH_2CH_2CH_2CH_2$	80
C_6H_5 CH_2-CH_2	70
cyclohexyl	70

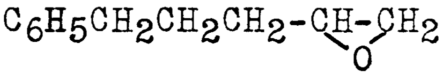
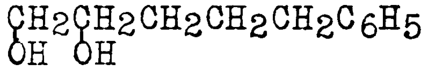
Studying α - A - copellidylheptyl alcohol, v. Braun found that



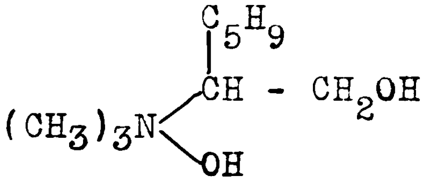
by distillation of the quaternary base in vacuum, about one third of the reaction gave methyl alcohol and the original amine-alcohol (above), while the larger portion gave Δ^1 heptene oxide and the N-methyl cyclic amine.

The substituted choline (88),

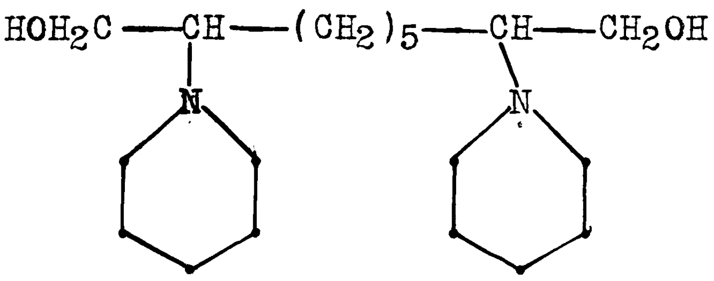


if heated in a vacuum was found to give about 40% of γ-phenylpropyl ethylene oxide  $C_6H_5CH_2CH_2CH_2\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2}$ about 30% of what appeared to be a polymer of this substance, and about 10% of the glycol  $\underset{OH}{CH_2}\underset{OH}{CH_2}CH_2CH_2CH_2C_6H_5$.

Another substituted choline - that from β- dimethylamino- β-cyclopentylalcohol

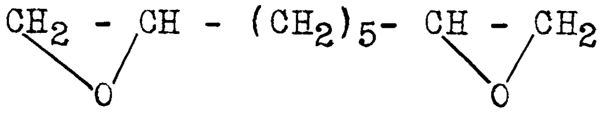


produced a little of the cyclopentylethylene oxide and a little of the glycol, but the yields were small. Starting with dibromosubstituted di-basic acids v.Braun and Münch were able to prepare compounds thought to be the bis-oxides. For instance ethyl α,α'- dibromoazelaate was converted to ethyl α,α'-dipiperidinoazelaate, which on reduction with sodium in alcohol yielded the alcohol

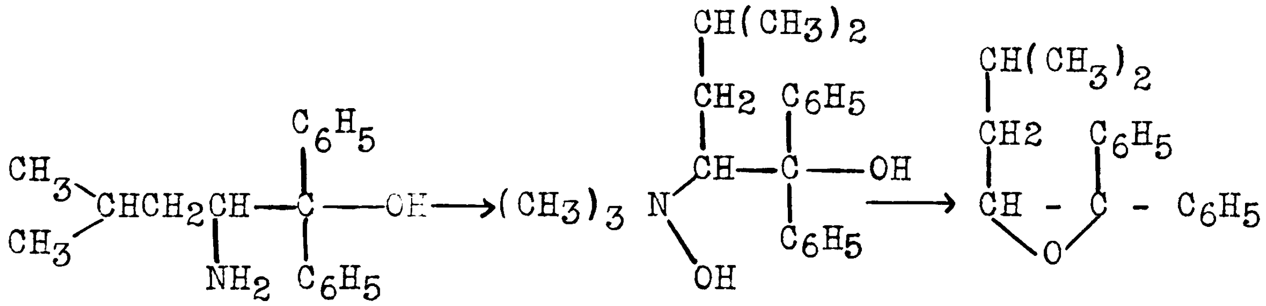


(88) v.Braun, J., Münch, W., Ber. 59 B. 1941-50 (1926).

this in turn on exhaustive methylation gave small amount of methylpiperidine and the bis oxide

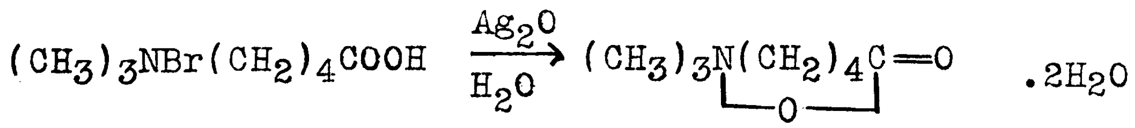


Still another substituted choline is that derived from 1-diphenylmethylaminopentanol (89), and which on heating produces the oxide with the opposite sign of optical rotation;



Betaines.

If from amino acids one tries to obtain the quaternary ammonium hydroxide, it has been found that frequently there appears instead the betaine. Willstätter (90), on treating the bromide of trimethylaminovaleric acid with moist silver oxide, isolated the corresponding betaine as a stable dihydrate.



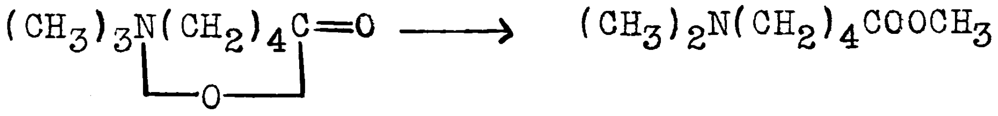
$$(CH_3)_3NBr(CH_2)_4COOH \xrightarrow[H_2O]{Ag_2O} (CH_3)_3\underbrace{N(CH_2)_4C}_{O}{=}O \quad \cdot 2H_2O$$

The betaine, on pyrolysis exhibited the usual reactions of long

(89) Kanao, S., Yaguchi, T. J. Pharm. Soc. Japan 48 358-66(1928). Chem. Abs. 22 3407 (1928).

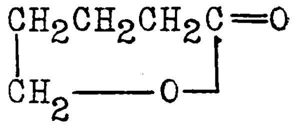
(90) Willstätter, R. , Kohn, W., Ber. 37 1853-58 (1904).

chain amino acid betaines (91), namely, that of being transformed into the isomeric ester of the dialkylamino acid.



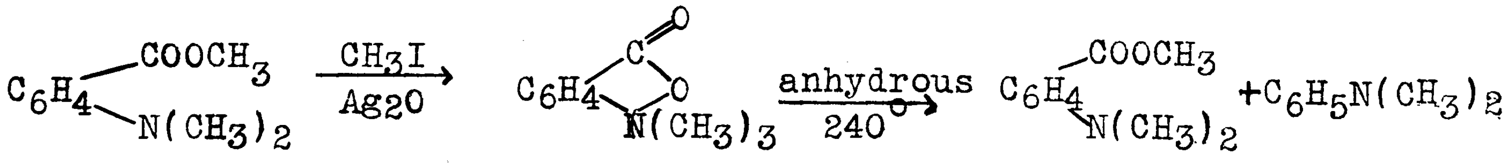
$$(CH_3)_3N(CH_2)_4C{=}O \longrightarrow (CH_3)_2N(CH_2)_4COOCH_3$$

This process of betaine formation is analogous to the esterification of acids with quaternary bases and in a way is again analogous to the inner esterification of hydroxy acids when they undergo lactone formation. The pyrolysis of the particular betaine above, yielded, besides the amino ester, a small amount of trimethylamine and a δ- lactone



$$CH_2CH_2CH_2C{=}O$$

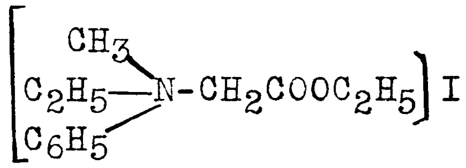
In the aromatic series, the same kind of thing occurs Willstätter and Kohn (92) treated o-dimethylamino-methylbenzoate with methyl iodide and silver oxide and obtained thereby, the corresponding betaine. This decomposed at 240°, chiefly to regenerate the original tertiary amine ester, but gave as well, a little dimethyl aniline, a reaction which predominated when water was present.



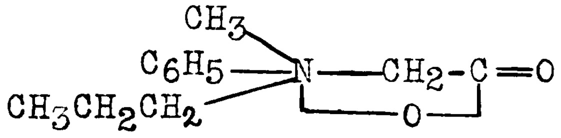
When different alkyl groups were present on the nitrogen in the betaine, Willstätter (93) supposed it was always the smallest one

(91) Kuhn, R., Giral, F. Ber. 68 B. 387-396 (1935).
(92) Willstätter, R., Kohn, W., Ber. 37 401-417 (1904).
(93) Willstätter, R., Ber. 35 584-620 (1902).

which passed into the carboxyl group to give the ester. It has recently been shown, however, that the behaviour is not quite so simple as this. The ammonium iodide (94)



on treatment with moist silver oxide, gave two different forms of the betaine, the one, a "metastable monohydrate", the other a "stable dihydrate". When the former was heated at 100-110° at 16 mms. for 24 hours, followed by a final heating at 180-90°, methylethylphenylamine, water, and N-methyl-N-phenyl ethyl acetate were obtained; the latter betaine hydrate on heating to 70-80° at 17 mms. then raising the temperature to 200-205° gave the same methylethylphenylamine, but the isomeric ester N-ethyl-N-phenylmethyl acetate. The betaine,



was also prepared in the form of two different hydrates, and although these on heating did not show the formation of different isomeric esters, at least to the same extent as in the first case, still it may be noted that from both, the propyl ester, and not the methyl was the one obtained; the heating of the dihydrate resulted in the formation of a little of the methyl ester, but the propyl predominated.

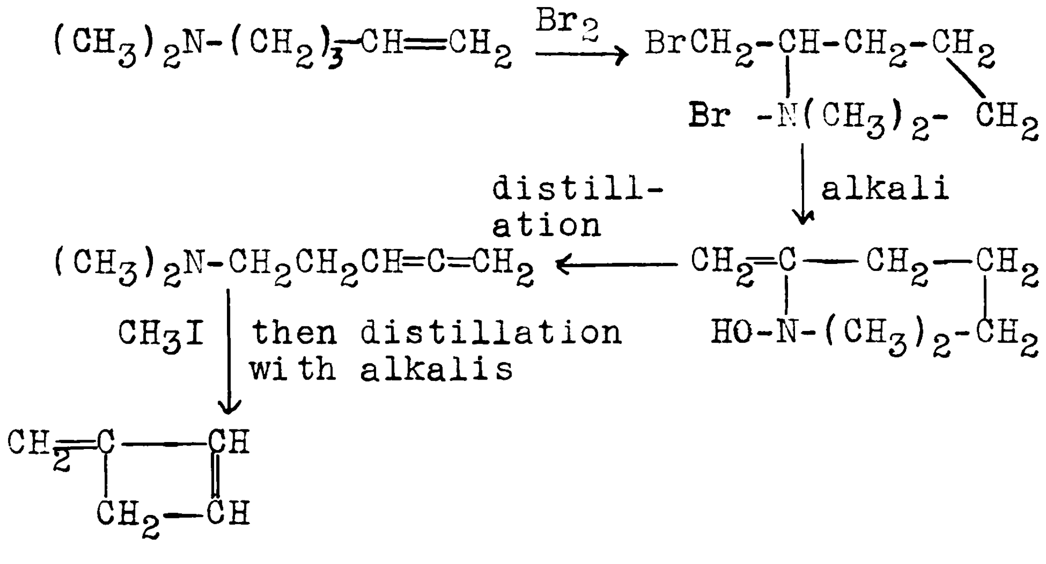
(94) Guaisnet-Pilaud, M., Ann.chim.(11) 4 365-448 (1935).

Two interesting synthesis accomplished by v.Braun and co-workers with the aid of the exhaustive methylation process, were the preparation of N-methylvinylaniline (95), and of pirylene (96). Until that time, no primary, secondary or tertiary amine was known which undoubtedly possessed a vinyl group on the nitrogen. Starting with methyl- (2-bromoethyl)-aniline and trimethylamine, the quaternary bromide was formed by allowing the components to react slowly in cold concentrated alcoholic solution, and using only the pure, crystalline material which had separated after three days. The bromide was treated with moist silver oxide in the usual way, the silver iodide and excess oxide removed by filtration, and the aqueous solution of the base evaporated to dryness. Then by distilling the hydroxide below 25 mms. pressure at 130-5°, N-methylvinyl aniline was produced.

v.Braun's synthesis of pirylene, though not original work nevertheless was of value since he proved the structure of the various compounds involved, and indeed, of pirylene itself. It had been known from the time of Hofmann that piperidine on exhaustive methylation, underwent ring opening, to give the so-called "dimethyl piperidine"; from this, by the action of bromine or iodine,Willstätter (97) obtained a

(95) v.Braun, J., Kirschbaum, G. Ber. 52B 2261-5 (1919).
(96) v.Braun, J., Teuffert, W., Ber. 61B 1092-9 (1928).
(97) Willstätter, R., Ber. 33 365-379 (1900).

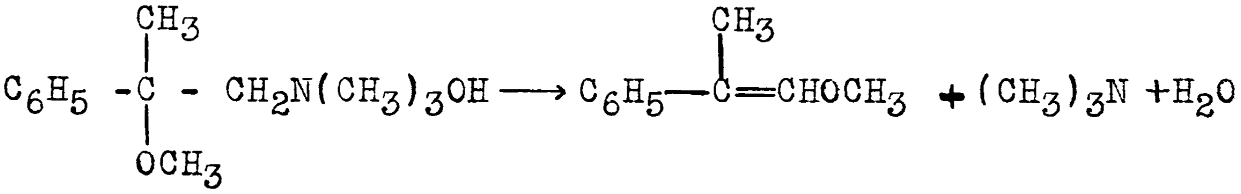
pyrrolidine derivative, which he subjected twice more to exhaustive methylation, thereby producing pirylene. It remained for v.Braun to show that the compound was a cyclobutene derivative, and not an open chain allene, as Willstätter assumed. The steps in v.Braun's synthesis are indicated below.



pirylene

It may be pointed out, that the last step of this synthesis, involving as it does the closure of a ring on decomposition of a quaternary ammonium base, is most unusual.

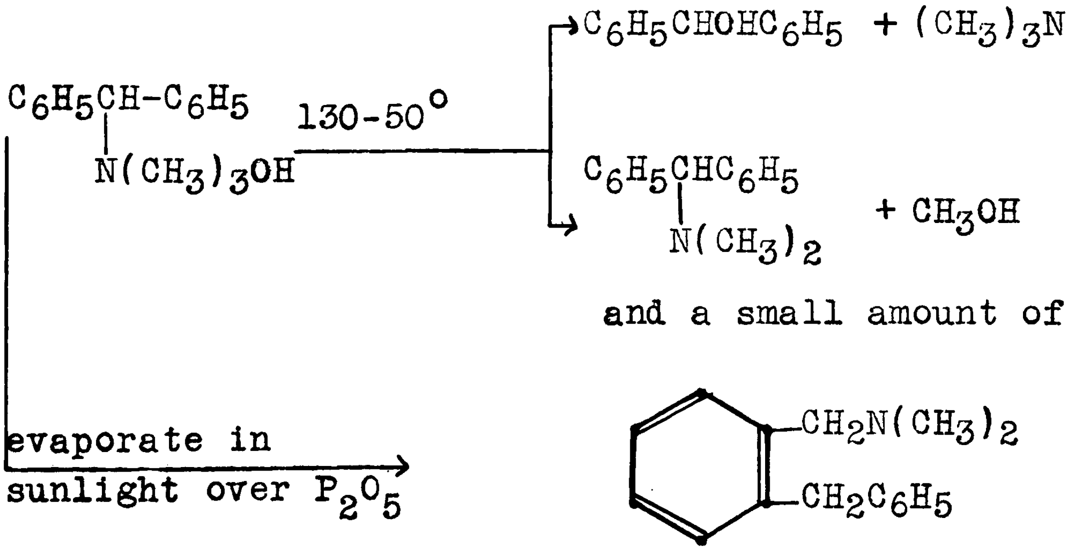
In the decomposition of quaternary ammonium hydroxides considered so far, with a few exceptions like the occurrence of camphene along with bornylene from trimethylbornylammonium hydroxide, there have been no instances of the appearance of rearranged products whose formation one might not predict as a result of the particular experimental conditions. There are however, two or three other unusual cases, for which no very adequate explanation has been advanced. One of these was observed by Tiffeneau (98), when he found that the "choline ether" decomposed in the manner shown by the equation:



$$C_6H_5-\overset{\displaystyle CH_3}{\underset{\displaystyle OCH_3}{C}}-CH_2N(CH_3)_3OH \longrightarrow C_6H_5-\overset{\displaystyle CH_3}{C}{=}CHOCH_3 + (CH_3)_3N + H_2O$$

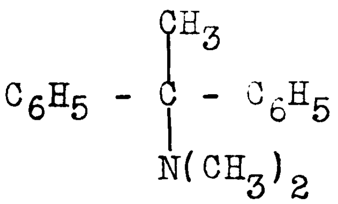
Here the methoxy group has migrated from one carbon to the other.

The second case occurred with the quaternary base from benzhydrylamine (99). When heated at 130-50°, it gave trimethylamine and benzhydrol, and also methyl alcohol and N,N-dimethyl - (diphenylmethyl) amine, as expected; but there appeared, as well a small amount of N,N-dimethyl-o-benzyl-benzylamine. If the aqueous solution of the base were evaporated in sunlight over phosphorus pentoxide, then the decomposition proceeded chiefly to give the rearranged amine, presumably through dehydration of the base, followed by rearrangement.



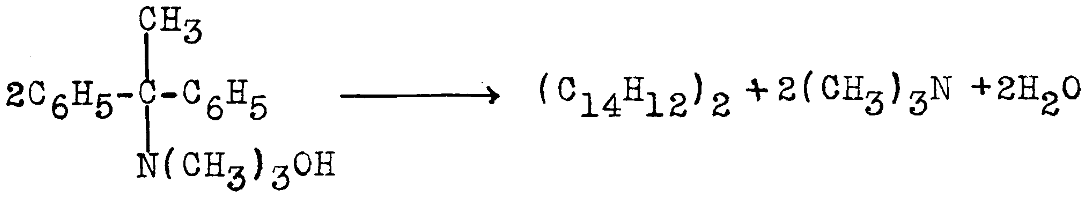
(98) Tiffeneau, M., Compt. rend. 158 1580-2 (1914).
(99) Sommelet, M. , Compt. rend. 205 56-8 (1937).

Somewhat earlier Hughes and Ingold (100) had carried out the same decomposition, reporting the formation, not only of the expected benzhydrol and benzhydryldimethylamine, but also of dibenzhydryl ether and benzhydrylmethyl ether; these latter compounds occurred only in small amounts and were considered to be produced by secondary reactions of benzhydrol. In addition to these, however, there was a third main product, $C_{16}H_{19}N$, to which Ingold assigned the structure



$$C_6H_5 - \overset{\displaystyle CH_3}{\underset{\displaystyle N(CH_3)_2}{C}} - C_6H_5$$

From this product, on distillation of its quaternary base, there should have been obtained 1,1-diphenylethylene, but instead there appeared a new crystalline dimeride of diphenylethylene.



$$2C_6H_5-\overset{\displaystyle CH_3}{\underset{\displaystyle N(CH_3)_3OH}{C}}-C_6H_5 \longrightarrow (C_{14}H_{12})_2 + 2(CH_3)_3N + 2H_2O$$

Sommelet has shown, by synthesizing (101) Ingold's N,N-dimethyl-1,1-diphenylethylamine and comparing it with the amine from his decomposition of benzhydryltrimethylammonium hydroxide, that the two products were not the same. Moreover, the latter amine must be N,N dimethyl-o-benzylbenzylamine,

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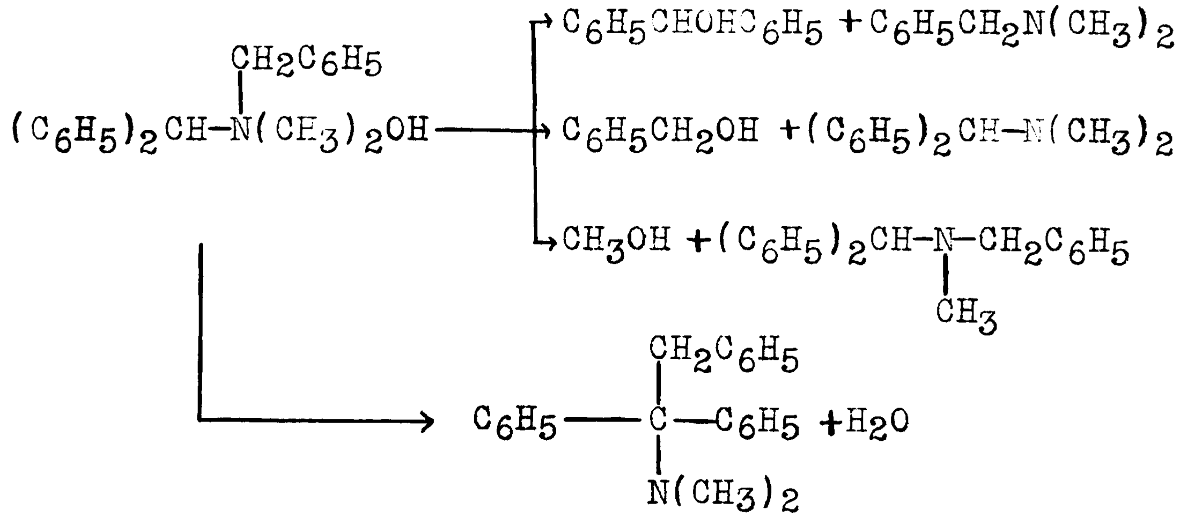
(100) Hughes, E.D., Ingold, C.K. J. Chem. Soc. <u>1933</u> 69-75
(101) Sommelet, M. Compt. rend. <u>183</u> 302-304 (1926).

since on treatment with acetic anhydride, Sommelet obtained acetyldimethylamine (showing the presence of an $-N-(CH_3)_2$ group) and an acetate; the acetate, on hydrolysis, gave o-benzylbenzyl alcohol, which was identified through oxidation with chromic acid in the cold to o-benzylbenzoic acid.

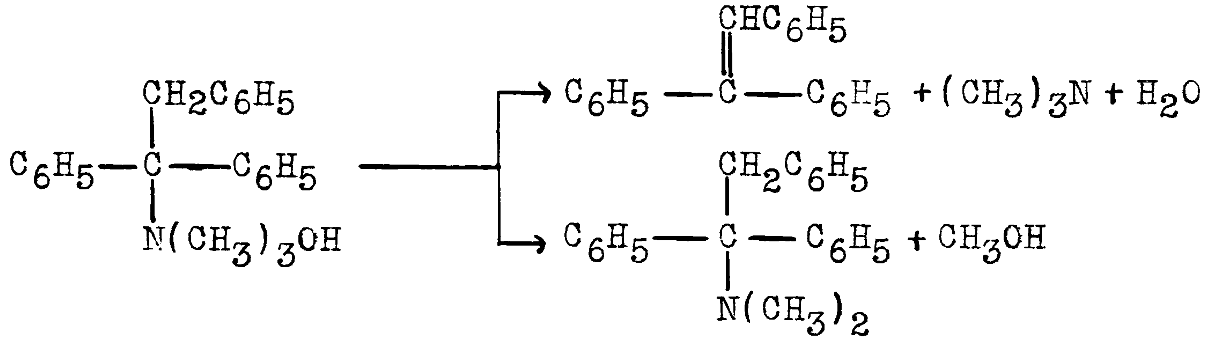
Hughes and Ingold, in assigning the structure N,N dimethyl-1,1-diphenylethylamine to the product from the decomposition of the quaternary base from benzhydrylamine had reasoned by inference from the behaviour of benzhydrylbenzyldimethylammonium hydroxide. This base decomposed in three normal ways, and in a fourth way that was shown to involve migration



$$(C_6H_5)_2CH-\overset{\overset{CH_2C_6H_5}{|}}{N}(CH_3)_2OH \rightarrow \begin{cases} C_6H_5CHOHC_6H_5 + C_6H_5CH_2N(CH_3)_2 \\ C_6H_5CH_2OH + (C_6H_5)_2CH-N(CH_3)_2 \\ CH_3OH + (C_6H_5)_2CH-\underset{\underset{CH_3}{|}}{N}-CH_2C_6H_5 \end{cases}$$

$$\rightarrow C_6H_5-\overset{\overset{CH_2C_6H_5}{|}}{\underset{\underset{N(CH_3)_2}{|}}{C}}-C_6H_5 + H_2O$$

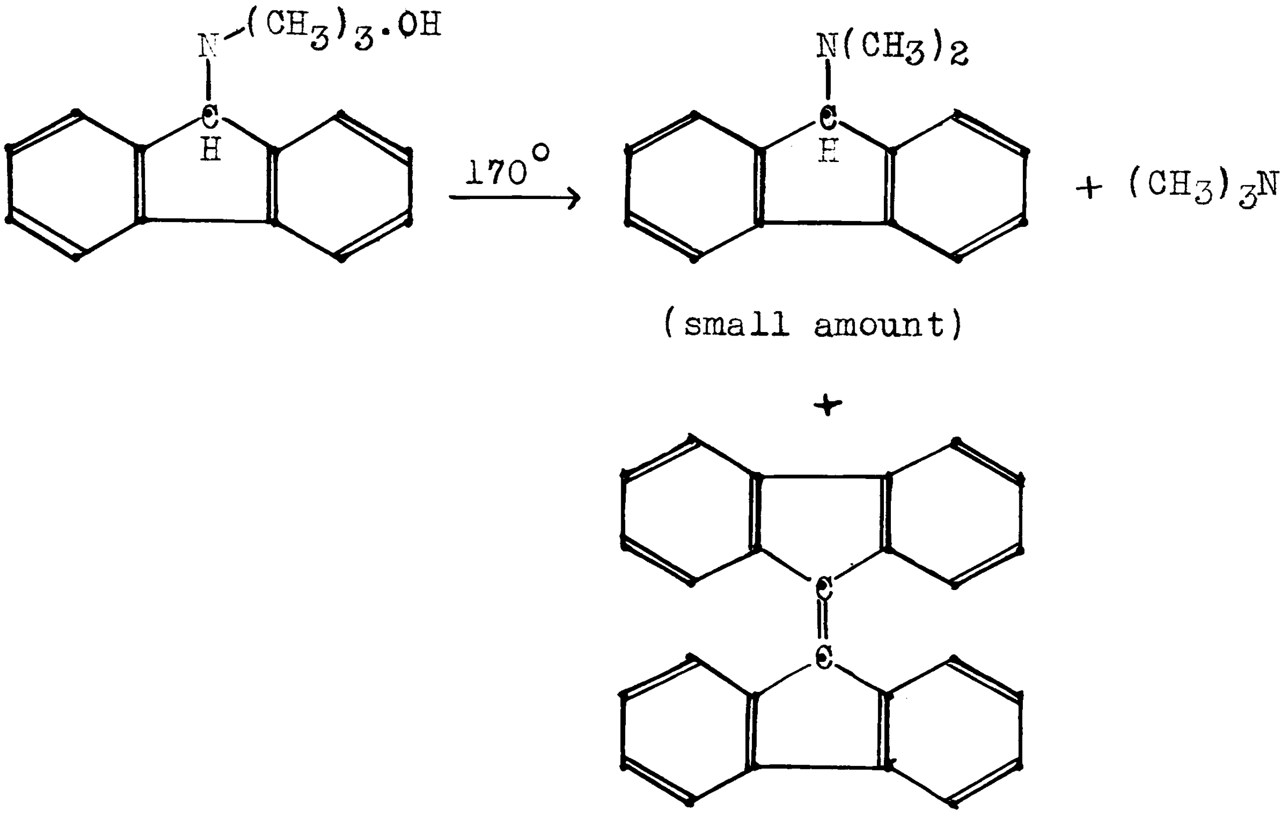
The structure of this latter product, from the abnormal decomposition was established by the identification of the products from the decomposition of its quaternary base.



The curious point in this work on the decomposition of the quaternary base from benzhydrylamine is that these two authors should each have carried out the decomposition, and each have obtained in fairly high yields, two entirely different products. Both advance good evidence in support of the assigned structure and neither appears to have found the compound reported by the other.

A final interesting and unusual ammonium base (102) studied by Ingold was that from fluoryl - 9 - dimethylamine; this hydroxide decomposed at 170°, to yield a small amount of dimethyl-9-fluorylamine and a high yield of trimethylamine; part of the corresponding 9-hydroxyfluorene appeared as the 9-fluoryl ether, but the major portion was recovered as bis-o,o-diphenylylene-ethylene (difluorylidene). Since this hydrocarbon was not formed from 9-hydroxyfluorene or the fluoryl ether under conditions similar to those in the experiment, the authors concluded that it must have been a primary product of the reaction.

(102) Ingold, C.K., Jessop, J.A., J. Chem. Soc. 1929 2357-61.



Fluoryl-9-triethylammonium hydroxide, except that it gave, no detectable amount of diethyl-9-fluorylamine, behaved in the same way, and these examples seem to be the first case of 1,1 elimination in the degradation of quaternary ammonium hydroxides.

And so, with these few exceptions out of a host of quaternary ammonium compounds, decomposition leadsto the formation of a tertiary amine, an alcohol or an olefin, the individual results depending on the size and type of the four groups attached to the nitrogen. Before going on to a consideration of the possible mechanism of this decomposition, it is desirable to review the organic esters of carbinols, and particularly the xanthates, that other class of compounds whose elimination reactions resemble those of the quaternary ammonium hydroxides in that rearrangement rarely, if ever occurs.

XANTHATE ESTERS.

Preparation and Properties.

The second large class of organic compounds to undergo elimination reactions without rearrangement of the remaining carbon skeleton, as has been mentioned earlier, are the xanthate esters. These are substances of the type R.O.C-SSR and the methyl esters, $R.O.CSSCH_3$, and were discovered in 1824 by Zeise (103); they are derivatives of the theoretical sulphothiocarbonic acid HO.CSSH - a compound not known in the free state. The first stable derivative is xanthic acid, C_2H_5OCSSH, and even this decomposes at 25° to alcohol and carbon disulphide; the alkali metal salts of this acid however, C_2H_5OCSSK, prepared by the combined action of carbon disulphide and potassium hydroxide in alcoholic solution are comparatively stable and may be obtained in the form of yellow, silky needles. The name xanthate is derived from the Greek and refers to the yellow colour of the precipitate formed between cupric salts and solutions of the alkaline xanthates. The action of methyl iodide on the alkaline xanthate produces the methyl xanthate ester,

From the time of their discovery in 1824 until 1899, little attention seems to have been paid to the xanthates.

(103) Richter, V. Organic Chemistry 1 (Allott E.N.) Kegan Paul, Trench, Tribner Co. Ltd., London p 489.

In that year however, L.A. Chugaev (104) first applied the reaction which later came to bear his name to the preparation of menthene from menthol, via the methyl xanthate ester. The method was quickly recognized as a most useful one for the preparation of olefins from corresponding carbinols, and has been widely used since, particularly in the field of terpene chemistry.

The original method, and the one that is still most frequently used for the preparation of the xanthate, was to dissolve the carbinol, in this case menthol, in dry toluene, to add slightly more than one equivalent of sodium and reflux until the sodium had practically all dissolved. It has been found (105) that in the case of carbinols whose metallic derivative is rather difficult to obtain, an advantage was gained by the use of the more active metal, potassium. A method recently recommended by Whitmore (106) has been to heat the alcohol with equimolecular quantities of sodium or potassium hydroxide and carbon disulphide, thus forming the xanthate in one step in a larger yield than was obtained by the original method. Excess alcohol,or equimolecular quantities of alcohol and some neutral solvent like diethyl ether and carbon tetrachloride may be used to provide the solvent.

(104) Chugaev, L.A. Ber. 32 332-335 (1899).

(105) Chugaev, L.A. J.Russ. Phys. Chem. Soc. 36 1253-58 (1904).

(106) Whitmore, F.C., Simpson, C.T. J. Amer. Chem. Soc. 55 3809-12 (1933).

Once the sodium alcoholate had been formed in the original method the unreacted sodium was removed and an excess (at least three times the theoretical amount) (107) of carbon disulphide added, followed shortly by an excess of methyl iodide. The inorganic salts were removed by filtration, the toluene by distillation in vacuum, and the methylmenthyl ester obtained as a low melting, crystalline solid. On dry distillation, it decomposed to menthene, carbonoxysulphide and methyl mercaptan.

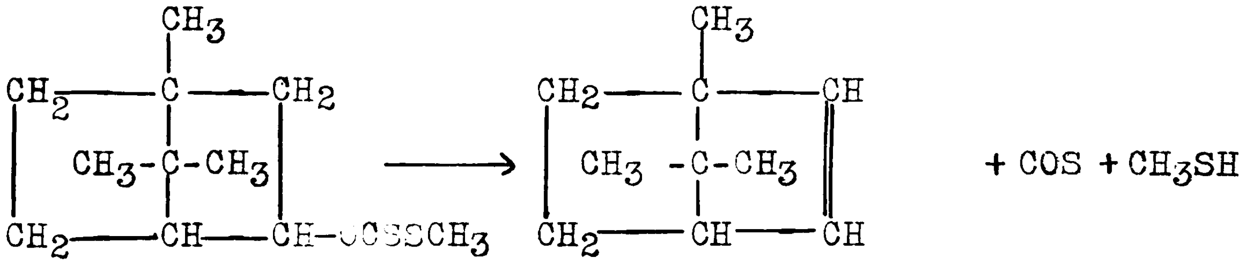
Chugaev tried also the effect of decomposing the dixanthate $ROCS_2CS_2CR$ of menthol, produced by condensing sodium menthylxanthate with iodine; although this gave menthene too, the yields were smaller, and this modification of the method was abandoned in favour of the former.

Pyrolysis of Methyl Xanthate Esters.

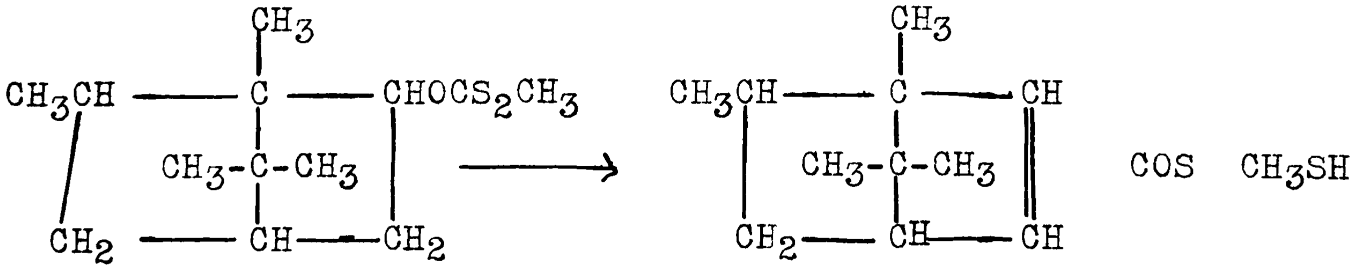
Shortly after the preparation of menthene from the methyl xanthate, Chugaev (108) announced the production of d-bornylene by the same method of pyrolysis of the methyl xanthate of l-borneol and this manner of preparation has been used by numerous workers since then. In the menthene, obtained not only from methylmenthylxanthate but also from ethylmenthylxanthate, Chugaev (109) was unable to find any trace of an impurity - or evidence of the non-homogenity of the product. The bornylene had not undergone any racemization

(107) Henderson, G.G. Caw. W. J. Chem. Soc. 101 1416-20 (1420)(1912).
(108) Chugaev, L.A. J. Russ. Phys. Chem. Soc. 32 332 (1900).
(109) Chugaev, L.A. J. Russ. Phys. Chem. Soc. 35 116-79 (1903).

and contained no impurities other than a little tricyclene. Later workers (110) have reported that the bornylene prepared by Chugaev's method, even after most careful purification contained as much as 25% tricyclene. The formation of a tricyclic hydrocarbon has been encountered fairly frequently in terpenes produced by the xanthate method, and as will be shown later, is one of the products normally to be expected. Its formation would seem to be a question of steric relationships for methylepibornylxanthate (111) decomposed to l-bornylene with no evidence of tricylene formation at all.



In the same manner, 6-methylborneol (112) on xanthate dehydration, gave only 6-methylbornylene:



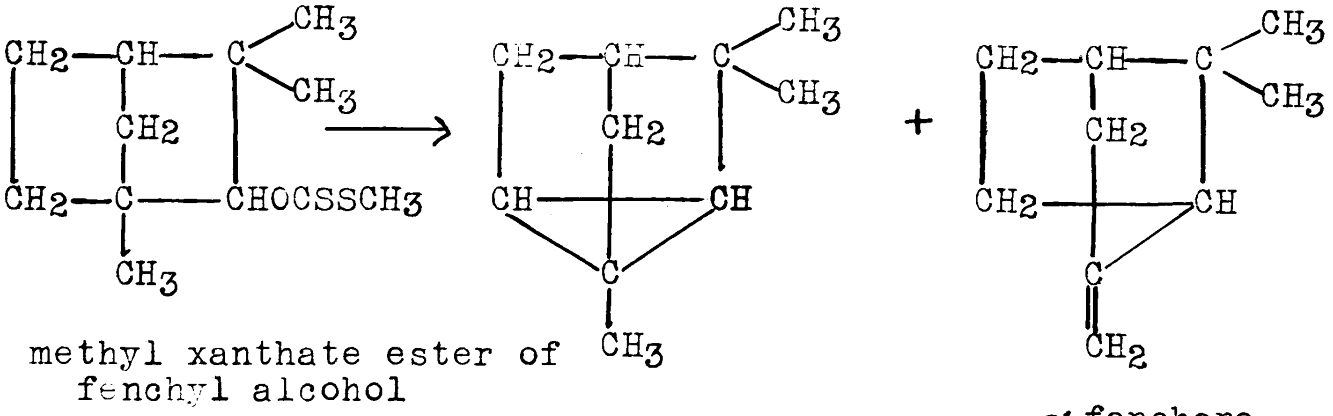
(110) Shriner, R.L., Sutherland, H. J. Amer. Chem. Soc. 60 1314-1320 (1938).

(111) Bredt, J., Perkin, W.H. J. Chem. Soc. 103 2182-2225 (2224) (1913).

(112) Bryusova, L. Ya. J. Russ. Phys. Chem. Soc. 59 653-8 (1927).

and 4-methylborneol, and 4-methylisoborneol (113), the same 4-methylbornylene, with no tricyclic isomer reported.

In the fenchene series, the formation of a tricyclic compound on decomposition of the xanthate ester is again encountered. Thus, by heating either the methyl or ethyl xanthate (114,115) ester at 150°- 230°, both decomposed as shown, to give (besides carbon oxysulphide and methyl mercaptan), cyclofenchene, and α-fenchene, but no β or γ isomers.



In most cases where there is more than one β-position to the xanthate group possessing available hydrogen, the isomers resulting from loss of either hydrogen are found to occur . Thus, Chugaev (116) showed that from the distillation of d-methyldihydrocarvylxanthate, he obtained both l-limonene, and l-isolimonene.

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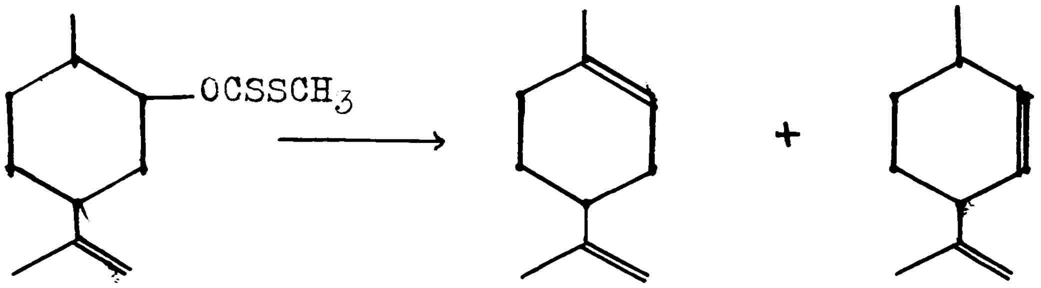
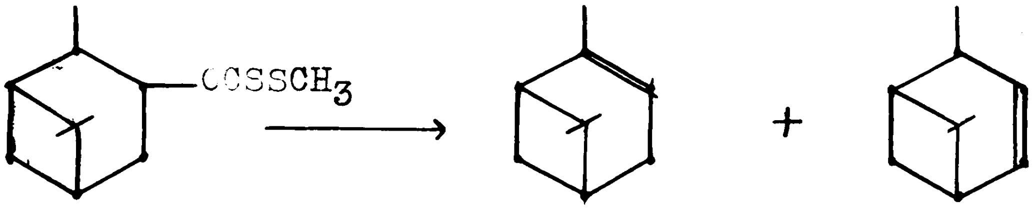
(113) Shavrygin, A.I. J. Gen. Chem. (U.S.S.R) 7 2754-9 (1937).
(114) Nametkin, S.S., Selivanov, A., Ruzhentzev, A., J. prakt. Chem. 106 25-38 (1923).
(115) Komppa, G., Nyman, G.A., Ann. 535 252-66 (1938).
(116) Chugaev, L., J. Russ. Phys. Chem. Soc. 36 988-1052 (1904).



d-methyldihydrocarvylxanthate　　1-limonene　　1-isolimonene

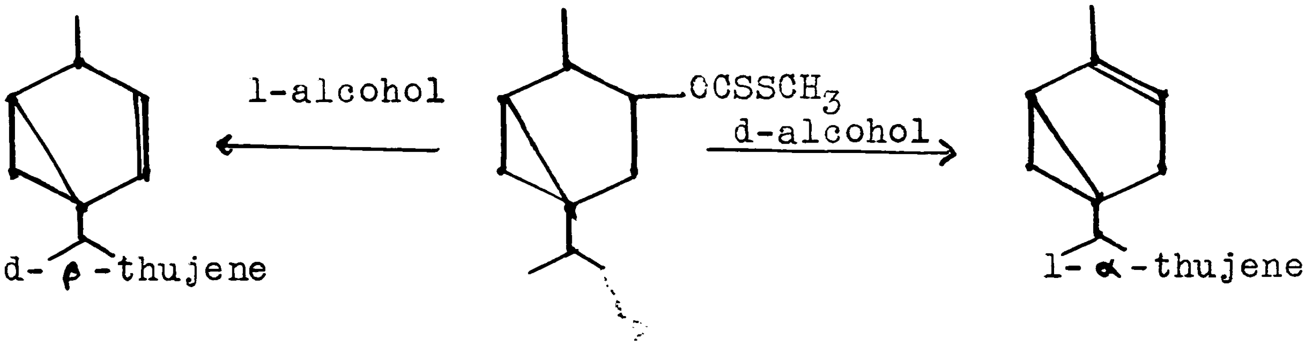
In the same way, distillation of methylpinocamphylxanthate (117) gave a mixture of α and δ pinenes.



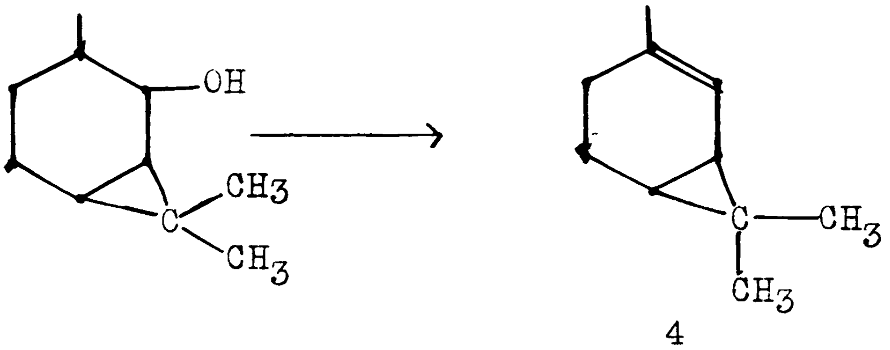
α pinene　　δ pinene

Numerous other hydrocarbons have been prepared in exactly the same manner from the corresponding terpene alcohol, and in most cases, where two or more β - hydrogen atoms were available, two or more isomers appeared, in varying amounts. Thus methylthujylxanthate (118) gave α, and β thujene. If the ester from pure d-thujyl alcohol were decomposed at 138°, the hydrocarbon obtained was practically pure 1-α-thujene - while the ester of 1-thujyl alcohol decomposed at 183° to give mainly d-β-thujene.

(117) Chugaev, L. J. Russ. Phys. Chem. Soc. 39 1324-43 (1907).
(118) Chugaev, L., Fomin, W. Ber. 45 1293-8 (1912).

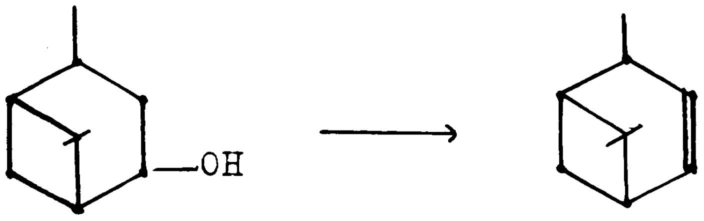


Two other hydrocarbons prepared more recently were Δ^4-carene from l-methylcarylxanthate (119)



l-carol Δ^4-carene

and l -δ- pinene from verbanol (120)



In these cases, only one isomer appeared, although there were two β-positions with apparently available hydrogen. The fact that only one isomer was found was a confirmation of Bredt's Rule (121) which stated that (122) "substances having an ethylenic linkage attached to a dicyclic ring, were extremely

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(119) Menon, K.N., Simonsen, J.L., J. Indian Inst. Sci. 10 A 1-5 (1927).

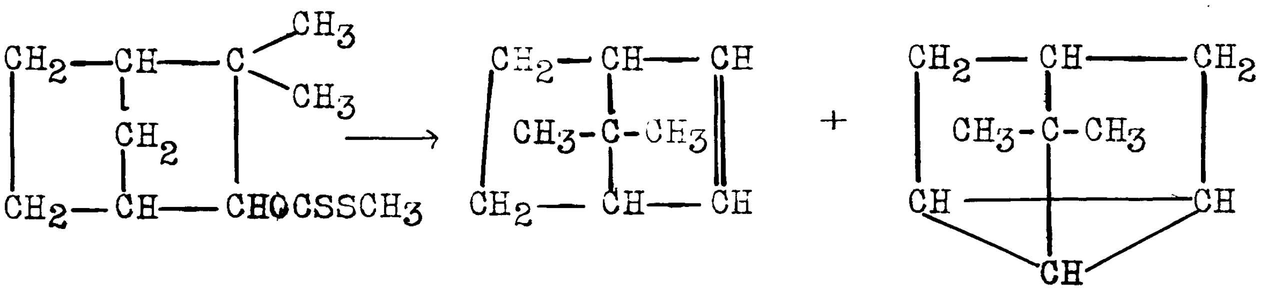
(120) Wienhaus, H., Schumm, P., Z.angew. Chem. 39 138 (1926).

(121) Bredt, J. Ber. 35 1206- (1902).
" J.prakt. Chem. ii 95 132 (1917).

(122) Simonsen, J.L., The Terpenes, 2 Cambridge Univ. Press (1932) p. 154-5.

unstable and tended to isomerize to a more stable form".

One curious reaction product, which on first sight would appear to have resulted from a Wagner rearrangement, was the occurrence of apobornylene along with apocyclene in the pyrolysis of methyl-camphenlylxanthate (123). Again as predicted by Bredt's rule, none of the isomer resulting from loss of the only hydrogen in the β position was found.



McAlpine (124) has studied the hydrolysis and decomposition of methylmenthyl xanthate and of methyl bornyl xanthate. She found that aqueous potassium hydroxide had little effect in bringing about the hydrolysis of either of these xanthates - in contrast to its action on methyl isobornyl xanthate, which as Chugaev (116) had found, was hydrolysed easily by potassium hydroxide, the isoborneol so formed undergoing dehydration to camphene in the course of the reaction. Alcoholic potash, as McAlpine observed, readily effected the hydrolysis of these esters to menthol and borneol, respectively; with alcoholic barium hydroxide, a partial hydrolysis was ac -

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(123) Komppa. G., Roschier, Ann. 429 175-(1922).
(124) McAlpine, I.M., J. Chem. Soc. 1931 114-21 .

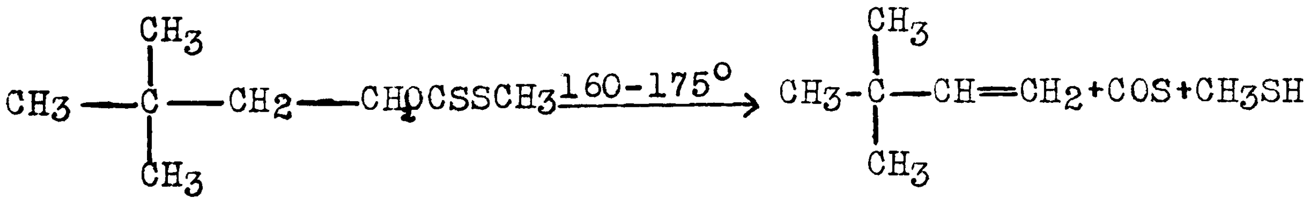
complished, with the accompanying transformation of some of the otherwise unchanged xanthate to a more stable form - a form which subsequently offered greater resistance to decomposition.

The thermal decomposition was studied under three sets of conditions, with slightly different results:
(a) the dry ester was heated alone, water being excluded;
(b) the ester was distilled in a vacuum; and (c) a solution of the ester in various solvents was heated. Under all conditions, the menthyl ester decomposed at least 30° below the bornyl ester. The effect of solvents on the decomposition was studied by heating 10% solutions of the esters at 120° for given periods; in all those solvents investigated, the products of the decomposition were menthene and bornylene (the latter containing some camphene) with the exception of ethylene dibromide, in which solvent, diterpenes resulted. Not all were equally effective in promoting the decomposition however, xylene, pyridine and n-butyl alcohol being among those in which slight decomposition occurred, and in which the xanthate was merely transformed into a substance identical in analysis, molecular weight, and physical properties, with the original ester, but differing from it in possessing an increased thermal stability. Ethylene dibromide and nitrobenzene brought about a fairly high amount of decomposition of the menthyl ester, but the former solvent was far more effective than the latter in decomposing the bornyl ester. With nitrobenzene, it was observed that the higher the temperature used (up to 170°) i.e. the more rapid the decompos-

ition - the higher was the optical rotation of the resulting menthene. The effect was shown to be not a question of a shorter time for racemization to occur at high temperatures because under the conditions of the experiment, menthene was not racemized.

The effect of replacing the methyl group in methylmenthyl xanthate by the isopropyl group (125) was to increase the tendency towards the formation of the "stable" form of the ester, whereas the introduction of the benzyl group caused a decrease in the tendency towards formation of the stable modification and an increase in the rate of decomposition in organic solvents.

Possibly the first application of the Chugaev method of dehydrating carbinols outside the terpene field was made by Fomin and Sochanski (126) in 1913 when they prepared tert-butylethylene from methyl pinacolylxanthate.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CHOCSSCH_3\xrightarrow{160-175^{\circ}}CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2+COS+CH_3SH$$

Since that time there have been other isolated instances of the use of this reaction, as for example, Kursanoff's dehydration of benzhydrol (127) to tetraphenylethylene, and benzylcyclohexylcarbinol (128) to benzylidenecyclohexane;

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(125) McAlpine, I.M. J. Chem. Soc., 1932 906-912
(126) Fomin, V., Sochanski, Ber. 46 244-8 (1913).
(127) Kursanoff, D. J. Russ. Phys. Chem. Soc., Chem. Part. 60 No. 6 921-4 (1928).
(128) Kursanoff, D., Ber. 64B 2297-2301 (2300)(1931).

Stevens' (129) dehydration of dextro-2-methyl-3-ethoxybutanol-2 to dextro 3-ethoxy-2-methyl-butene-1; and Levene's(130) dehydration of 1-(2-methoxyethyl) cyclohexanol to 2-methoxyethylcyclohexene.

In 1933, Whitmore and Simpson (106) studied the xanthate dehydration reaction, and besides isolating the normal hydrocarbons from isoamyl, n-amyl and capryl alcohols, found that primary xanthates were much more stable to heat, and resisted thermal decomposition to a greater degree than did secondary and tertiary xanthates. Whitmore's modification of Chugaev's original method of preparing the sodium or potassium xanthate derivative has been mentioned earlier (p.70).

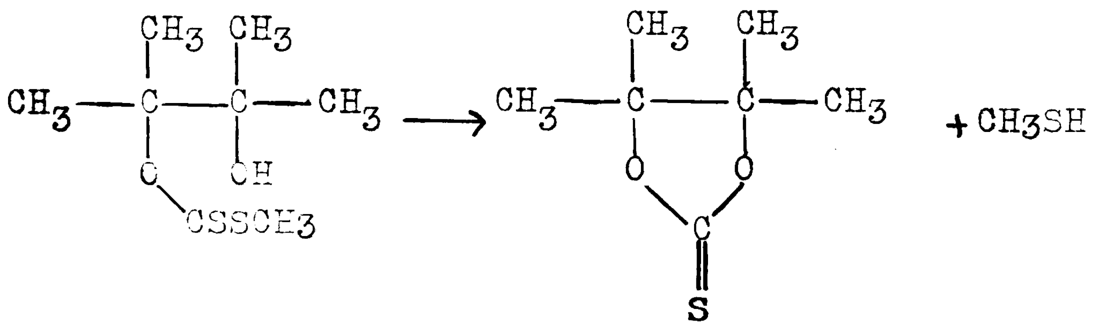
Shortly after this, Schurmann and Boord, in their (131) survey of the olefins of the hexane, heptane and octane series, applied the Chugaev reaction to the dehydration of certain carbinols and confirmed the earlier observation that in every case, the olefin produced consisted entirely of the non-rearranged form. Besides repeating the work of Fomin and Sochanski on the dehydration of pinacolyl alcohol, these authors prepared from the corresponding carbinols, 3,3 dimethyl-1-pentene; 4,4-dimethyl-2-pentene; 4-4 dimethyl-2-hexene and 2,2 dimethyl-3-hexene, each one being obtained in a high state of purity.

(129) Stevens, P.G., J. Amer. Chem. Soc., <u>54</u> 3732-38 (3736)(1932).

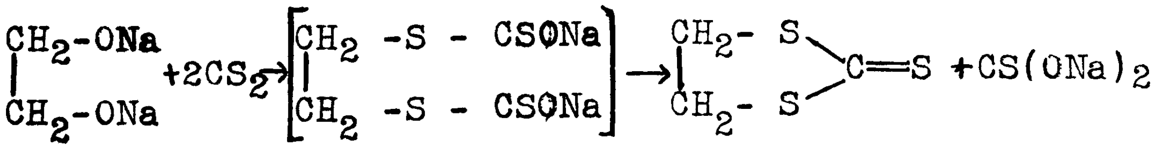
(130) Levene, P.A., Harris, S.A., J. Biol. Chem. <u>113</u> 55-9(1936).

(131) Schurmann, I., Boord, C.E. J. Amer. Chem. Soc. <u>55</u> 4930-35 (1933).

Fomin (132) has prepared the monoxanthate from pinacol, and found that this ester decomposed in the process of formation with the evolution of methyl mercaptan, but no carbon oxysulphide; the product so obtained proved to be an inner cyclic thio carbonate,



Other workers have studied the Chugaev reaction as applied to dihydroxy alcohols, attempting to make, not the monoxanthate as Fomin did, but the di-xanthate of the glycol. It was found (133) that the di-sodium salt of a glycol could readily be obtained by adding the glycol to a solution of sodium ethylate and distilling off the ethyl alcohol. The sodium glycolate failed, however, to yield a sodium xanthate derivative with carbon disulphide, there being found instead ethylene sulphocarbonate, probably through the decomposition of the unstable sodium derivative:



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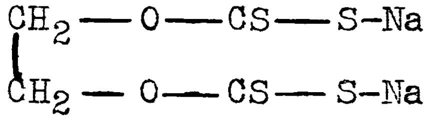
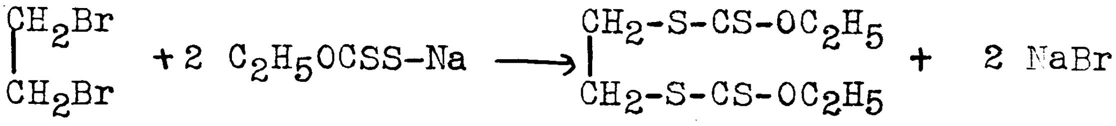
(132) Fomin, V.A., J. Gen. Chem. (U.S.S.R) 5 1192-4 (1935).
(133) Tischchenho, V.E., Kosternayo, A.F. J. Gen. Chem. (U.S.S.R.) 7 1366-77 (1937).
Kosternayo, A.F., Uchenye Zapiski Leningrad, Godsudarat. Univ. Ser. Khim. Nank. 3 126-56 (1938).
Chem. Abs. 33 3760 (1939).



Attempts to make the isomeric compound $\begin{array}{l} CH_2 - O - CS - S\text{-}Na \\ | \\ CH_2 - O - CS - S\text{-}Na \end{array}$ were unsuccessful, and the compounds finally studied were prepared by the interaction of the dibromide corresponding to the glycol, and sodium xanthate,



$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} + 2\ C_2H_5OCSS\text{-}Na \longrightarrow \begin{array}{l} CH_2\text{-}S\text{-}CS\text{-}OC_2H_5 \\ | \\ CH_2\text{-}S\text{-}CS\text{-}OC_2H_5 \end{array} + 2\ NaBr$$

These compounds decomposed in essentially the same manner as Chugaev's methyl xanthate esters, to yield, besides the appropriate hydrocarbon, carbon oxysulphide and ethyl mercaptan, with smaller amounts of hydrogen sulphide, diethylsulphide and diethyldisulphide.

Ethylene glycol, on dehydration in this manner, yielded acetylene; propylene glycol, from which both allene or methyl - acetylene might be expected, produced only methylacetylene; and from butane-2-glycol, butadiene was obtained with no dimethylacetylene.

And so, from the examples considered above, it will be seen that the xanthates, (and to a lesser extent, the benzoates and acetates) constitute a second class of organic compounds which undergo elimination reactions without rearrangement, - even in cases where the same organic residue, after elimination of other functional groups, rearranges almost entirely. The apparent exceptions to the general rule of non rearrangement on decomposition of quaternary ammonium hydroxides, and xanthate esters will be considered in the following section. The various mechanisms proposed for the decomposition of quaternary ammonium hydroxides will be reviewed, and in the light of new experimental evidence, certain modifications of existing views will be proposed. In addition, from original data on the decomposition of xanthate esters, a mechanism for this reaction will be advanced, for the first time; rearrangements hitherto reported as occurring in such decompositions will be shown as very probably due to secondary decomposition of a primary product of the reaction.

THEORETICAL DISCUSSION.

For many years following Hofmann's original discovery of the pyrolytic decomposition of quaternary ammonium hydroxides, other workers investigated the nature of the products from a large variety of these compounds, without enquiring particularly into the mechanism involved. It was recognized on purely empirical grounds, that if one of the four groups around the nitrogen were ethyl, that it would be preferentially eliminated as ethylene. Furthermore, the decomposition could proceed in two directions, in the one, to yield an olefin, water and trimethylamine, and in the other, to give a mixed tertiary amine and methyl alcohol. The extent to which the reaction followed either path depended on the nature of the groups attached to nitrogen.

In 1911, v.Braun (134) put forth his views on the question of this decomposition, but they too, were largely empirical, and were based on observations of a further series of quaternary hydroxides. Inasmuch as the decomposition took place at comparatively low temperatures, v.Braun believed the formation of an olefin to be a primary step in the reaction, and not due to the secondary elimination of water from an alcohol. The matter of symmetry of the olefin was important, and compounds from which a symmetrical olefin could be produced, decomposed largely in that direction. In

(134) v.Braun, J. Ann. 382 1-49 (1911).

the longer aliphatic radicals however, the terminal double bond would not be placed symmetrically, with the consequence that more of the reaction would go to produce methyl alcohol and mixed tertiary amine. On these grounds, n-butylethyldimethylammonium hydroxide would be expected to produce the very symmetrical ethylene, rather than the less symmetrical butylene, and such was found to be the case. A list of radicals arranged in order of their increasing tendency to be eliminated as an unsaturated hydrocarbon was drawn up and in this state the problem was left until 1927. In that year the theory of Hanhart and Ingold (135) was published and extended in 1933 by Hughes, Ingold and Patel (136).

These authors recognized the two general cases to be considered - either the production of an olefin, tertiary amine and water (hereafter called reaction A) and the production of a tertiary amine and an alcohol (hereafter called reaction B)

$$R_1R_2R_3R_4NOH \begin{cases} \rightarrow R_1R_2R_3N + \overset{?}{r_4} + H_2O & \qquad \underline{\underline{A}} \\ \rightarrow R_2R_3R_4N + R_1OH & \qquad \underline{\underline{B}} \end{cases}$$

In olefin production, Ingold concluded that it was always the hydrogen atom in the β-position to the nitrogen that was removed with the hydroxyl group to form water. The only alternative to this view was to suppose that an α- hydrogen was first removed, the resulting organic fragment with a bivalent

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(135) Hanhart, W., Ingold, C.K. J. Chem. Soc. <u>1927</u> 997-1020.
(136) Hughes, E.D., Ingold, C.K. Patel, C.S., J. Chem. Soc. <u>1933</u> 526-30.

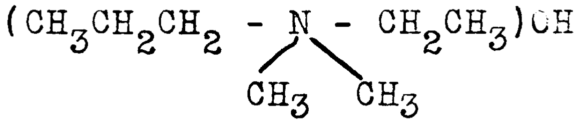
carbon atom at the end then undergoing rearrangement to give the olefin. Against this theory of α-elimination was the fact that ethylene (from the coupling of two CH_2 = fragments) had never been detected among the decomposition products of tetramethylammonium hydroxide, nor had stilbene been obtained from benzyltrimethylammonium hydroxide. Further proof that the β-hydrogen was the active one in the decomposition was furnished by observations (137) on the decomposition of bases not possessing any α-hydrogen - but which decomposed to give the expected olefin.

Assuming that the β-hydrogen was really the one to be eliminated, then in order to explain how the necessary reactivity was propagated to such a distant carbon atom through two intervening saturated carbon atoms without activating them en route, Ingold applied to this case, his earlier hypothesis (138) that hydrogen atoms in organic molecules, even those in hydrocarbon radicals, existed to a greater or less degree in a condition of incipient ionisation, depending on the electron affinity of the surrounding groups; under suitable conditions, as for example, attack by a reagent like an hydroxyl ion of great proton-affinity, the most incipiently ionised hydrogen - now assumed to be the beta one could be removed as a proton, and the electrons it left behind after such a break, be absorbed into the residue in a manner again determined by the electron-

(137) Kohn, Schlegl, Morgenstern, Monatsh. 28 491-525 (1907).
(138) Holmes, E.L., Ingold, C.K., J. Chem. Soc. 1926 1305-10.

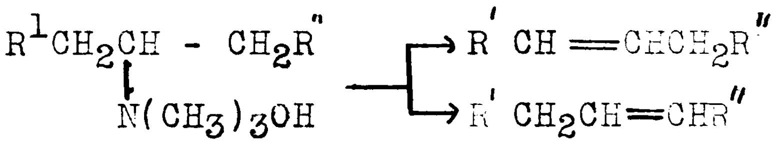
affinity of the groups present.

Applying this hypothesis to the case of a simple decomposition of a quaternary base, containing among other alkyl radicals, an ethyl group, it can be shown in theory, as well as in practice, that this is the group to be preferentially eliminated. Since an alkyl group repels its shared electrons more strongly than does hydrogen, in a compound like dimethylethyl-n-propylammonium hydroxide



the effect of the terminal methyl group of the propyl chain, by virtue of its greater ability to repel electrons, increases the electron density on the β-carbon of this chain, relative to the density produced on the β-carbon of the ethyl chain by the less effective terminal hydrogen atom. That is to say, the incipient ionisation of the β-hydrogen of the propyl chain is lessened relative to that of the β-hydrogen of the ethyl chain; accordingly,the extraction of the propyl proton by an hydroxide ion, with the dependent decomposition to yield water and propylene, is hindered relatively to the extraction of the ethyl proton to give ethylene and water. In a similar manner the elimination of the phenylethyl group from dimethylethylbenzylammonium hydroxide rather than the ethyl is explained by reason of the smaller electron repelling effect of the phenyl group - an effect really amounting to activation of the β - hydrogen by the phenyl group. This activation of the β - hydrogen may be so increased by substituents in the benzene ring, that in the attempted preparation of hydroxides containing the p-nitrophenylethyl group (135) (139), this group was lost immediately as p-nitrostyrene, and made the preparation even of the quaternary salts impossible.

In connection with this point, v.Braun and Hamann (140) have shown that in hydroxides were two β - hydrogens were available, the one rendered most active as a result of electron distributions of different neighboring groups will be the one to be eliminated



$$R^1CH_2\underset{\substack{|\\ N(CH_3)_3OH}}{CH} - CH_2R'' \longrightarrow \begin{cases} R'\ CH{=}CHCH_2R'' \\ R'\ CH_2CH{=}CHR'' \end{cases}$$

They found that by keeping R^1 = phenyl, and R'' = various para and meta substituted phenyl groups, that the degree of decomposition to give $R^1CH{=}CHCH_2R''$ could be altered as predicted by theory.

On the basis of their theoretical considerations, Ingold and co-workers predicted the manner of decomposition of a variety of other compounds, and were able to confirm this experimentally. From the results, a series was drawn up

$$CH_3CH_2CH_2 < H.CH_2CH_2 < C_6H_5CH_2CH_2 < NO_2C_6H_4CH_2CH_2$$

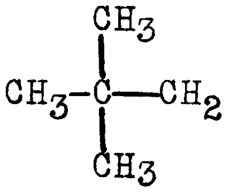
(139) Hughes, E.D., Ingold, C.K., Scott, A.D., J. Chem. Soc. 1937 1271-1277 (1273).

(140) v.Braun, J., Hamann, K., Ber. 65B 1580-6 (1932).

showing various groups arranged in increasing ease of elimination as olefins. The authors further pointed out that this series indicated not only the direction, but also the ease of decomposition. Decompositions leading to the splitting off of ethylene and propylene required fairly high temperature, while as has already been mentioned, those giving p-nitrostyrene took place during the attempted preparation of the quaternary compound, and made it impossible to isolate it.

Now the formation of an olefin, however, involves the carbon atom in the β- position to the nitrogen. If this atom carries no hydrogen, or if the ionisation of this hydrogen is hindered by the strong electron repulsion of neighboring groups, an olefin can not be formed, and an alcohol is eliminated instead. The nitrogen in this case must extract the shared electrons from one of the four groups; the depleted group is therefore eliminated as a positive fragment, which at once unites with any negative ion in the solution - thus giving rise here to an alcohol. Which of the four groups to be eliminated from $R^1R^2R^3R^4NOH$ depends naturally, on the relative stabilities of the four possible positive fragments, and as before a series of groups devoid of β - hydrogen may be found, arranged in order of decreasing ease of elimination as an alcohol:

$$(C_6H_5)_3C \quad (C_6H_5)_2CH \quad C_6H_5CH_2$$



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2$$

It will be noticed that this theory requires that the group with the greater tendency to separate as a cation should preferentially be eliminated as an alcohol. Yet it has been observed that in the case of trimethylneopentylammonium hydroxide (141) the decomposition yielded methyl alcohol exclusively, even though the electron-release from the tert.-butyl portion of the neopentyl radical should facilitate the formation of the corresponding cation, and hence, of neopentyl alcohol.

To overcome this difficulty, Ingold in the later paper (136) has pointed out that in such cases, reaction B, hitherto considered as a first order reaction, must be regarded as bimolecular and involves both the quaternary ammonium ion, and the hydroxide ion. Then in such a case, even though the neopentyl is the more stable cation, the electron release of the tert.-butyl portion of the group $[(CH_3)_3C \rightarrow CH]$ so increases the electron density on the α- carbon atom that attack by the hydroxyl group is hindered and a methyl group is lost instead.

This conception of the reaction however, is not entirely satisfactory, for it seems unnecessary to suppose that the hydroxyl group must attack the ammonium ion directly at the point of attachment of the group later to be eliminated from the nitrogen; and unless the attack must be made there it is difficult to see what influence the electron repulsion of the

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(141) Ingold, C.K., Patel, C.S. J. Chem. Soc. <u>1933</u> 67-68.

tert-butyl group could have on preventing the elimination of the neopentyl group as a cation. The conclusion is that the neopentyl group is not necessarily a more stable cation than methyl, nor is the electron density on the CH_2 group such as to encourage the loss of two electrons from the group with the consequent formation of a neopentyl cation.

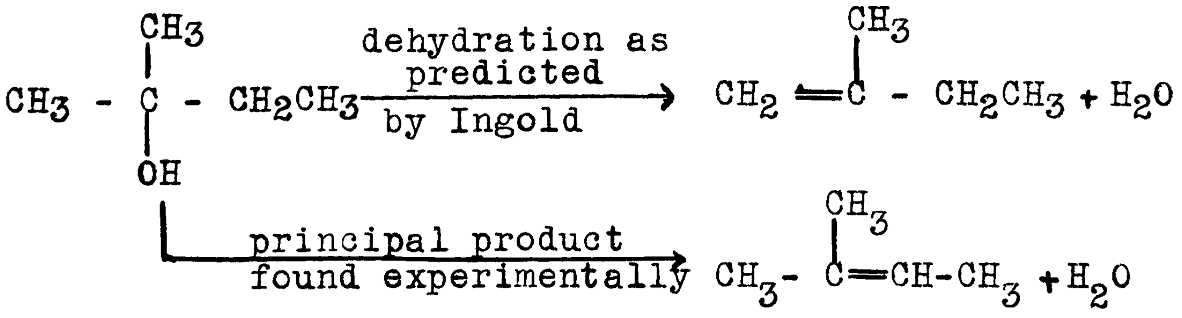
The results of Whitmore's work on neopentyl chloride (142) and iodide (143) confirm this view, and show that, contrary to Ingold's idea, these substances have an extraordinaryly high degree of stability. They react only slightly with such reagents as potassium cyanide, the sodium derivative of malonic ester, sodium ethylate or with dilute alcoholic potassium hydroxide.

Ingold has further stated that the tert.-butyl group in tert.-butyltrimethylammonium hydroxide is readily lost as the alcohol, a fact that must follow inevitably from the application of his views on electron release by various groups. The only experimental evidence however, from which alcohol formation was deduced was contained in the statement: (144). "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." The presence of a fairly

(142) Whitmore, F.C., Fleming, G.H. J. Amer. Chem. Soc. 55 4161-62 (1933).
(143) Whitmore, F.C., Wittle, E.L., Popkin, A.H., J. Amer. Chem. Soc. 61 1586-90 (1939).
(144) Hanhart, W., Ingold, C.K. J. Chem. Soc. 1927 997-1020 (1017).

large amount of trimethylamine in the basic constituents of the decomposition indicated that methyl alcohol was not produced in any great quantity, but the tert.-butyl group may well have been evolved as isobutylene - for which no search seems to have been made.

A further instance of the anomalies that result from too general an application of Ingold's electron repulsion theories, is to be seen in the dehydration of tert.-amyl alcohol (144a). This proceeds through the initial loss of the OH group as an anion, followed by ejection of a proton, and obviously the one to go should be the one most loosely held as a result of electronic influences of neighboring groups. According to Ingold, since a methyl group repels its shared electrons more strongly than does hydrogen, the ionisation of the β - hydrogen of the ethyl fragment should be hindered relatively to the ionisation of a β - hydrogen in one of the methyl groups. On these grounds one would therefore predict the dehydration to yield principally 2-methylbutene-1, whereas actually the chief product of the dehydration is 2-methylbutene-2.



$$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}} - CH_2CH_3 \xrightarrow[\text{by Ingold}]{\text{dehydration as predicted}} CH_2 = \overset{\overset{CH_3}{|}}{C} - CH_2CH_3 + H_2O$$

$$\xrightarrow[\text{found experimentally}]{\text{principal product}} CH_3 - \overset{\overset{CH_3}{|}}{C} = CH - CH_3 + H_2O$$

(144a) Hibbert, H., J. Amer. Chem. Soc. 37 1748-63 (1915).

Possibly an important factor in this reaction, as was suggested earlier by v.Braun, is the question of symmetry of the resulting olefin, the one with the most symmetrical structure, being the one to occur in largest amount.

v.Braun (145)(146) agreed in general with Ingold's theory of decomposition, though as a result of his experiments on the influence of glycerol and of potassium hydroxide on the mode of decomposition, he was inclined to regard reaction B - that is methyl alcohol formation, as a function of the unionised ammonium hydroxide. The glycerol, by repressing the ionisation, favoured reaction B; the potassium hydroxide was found to increase the amount of decomposition according to reaction A, and v.Braun argued that although the added hydroxide ions might also be expected to repress the ionisation, yet because the concentration of the molecular ammonium hydroxide was at best, only very small, the repression of ionisation effect must be small in comparison with the direct, accelerative effect of the added hydroxide ions on the ionic reaction A.

In reply to this, Ingold pointed out the fact that according to Sidgwick, the existence of quaternary ammonium hydroxides in other than the completely ionised state was impossible, and that hence no reaction involving the unionised form could be considered. Regarding the effect of added glycerol, Ingold attributed it's entire action to the form-

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(145) v.Braun, J., Teuffert, W., Weissback, K. Ann. 472 121-142 (1929).
(146) v.Braun, J., Buchman, E.R., Ber. 64B 2610-7 (1931).

ation of glyceroxides, which as v.Braun had mentioned, was a possibility. As to the potassium hydroxide, Ingold pointed out that the argument here was entirely contrary to Le Chatelier's principle; moreover, assuming for the moment that the quaternary hydroxide could exist in the unionised state, this form would presumably predominate in the fused ammonium hydroxide and lead to more methyl alcohol formation here than to olefin production - a fact not always observed in practice.

Leaving aside the finer details of the theory, the essential point in Ingold's mechanism of the decomposition of quaternary ammonium hydroxides with β - hydrogen available is that expulsion of this hydrogen as a proton occurs, followed by a rupture of the carbon nitrogen bond.

As alternatives to Ingold's theory, two possibilities are conceivable. The first of these is that the break between carbon and nitrogen occurs first, the nitrogen taking the pair of shared electrons, and the proton (from the β - position) is eliminated afterwards. Under these circumstances, the case would revert to the type encountered in the dehydration of carbinols, in which, by loss of an OH group, accompanied by its pair of shared electrons, the organic residue is left with an open sextet; then in such a system a rearrangement of the carbon skeleton could readily take place in the manner discussed by Whitmore in his paper entitled "The Common Basis of Intramolecular Rearrangements". (147).

(147) Whitmore, F.C., J. Amer. Chem. Soc. 54 3274-83 (1932).

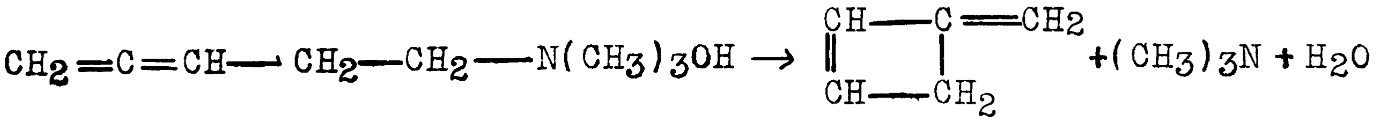
The second possibility is that the decomposition might involve a free radical mechanism - especially at the comparatively high temperatures required for the reaction to take place. However, in view of the fact that no products resulting from the disproportionation of such a free radical have generally been reported, this mechanism seems rather unlikely except possibly in a few special cases.

The mechanism for this elimination reaction as outlined by Ingold tacitly rules out the possibility of the occurrence of isomers of the expected olefin, i.e. of rearrangement. This follows directly from the assumption that proton expulsion occurrs before rupture of the carbon-nitrogen bond. When such a bond breaks, an open sextet is always formed, but due to preliminary loss of a proton, there is a lone pair of electrons available in the fragment. Stabilization can then be achieved by shift of this lone pair of electrons to form an ethylene bond, with so much less energy change than a shift of a group accompanied by its shared electrons, that the former change occurs . In any case, shift of a group would produce a α - γ dipole and could only lead to the formation of a cyclopropane derivative.

However, in the terpene series there are several cases of isomeric olefins occurring together with the expected normal dehydration product, and the question is whether these are primary or secondary products of the reaction; in the aliphatic series, it would appear that no careful search has ever been made for rearranged products in the evolved olefins, previous workers having assumed that none were produced. It has therefore seemed desirable to investigate the decomposition reaction more closely, with the object of distinguishing between the three possible mechanisms - Ingold's, which precludes the possibility of rearrangement, the second, in which the carbon-nitrogen bond breaks before the expulsion of the proton, thereby setting up a system in which rearrangement could occur, and finally, a free radical mechanism. With regard to Ingold's theory, it seems unnecessary to go to such lengths to explain the activity of the β-hydrogen atom and its incipient ionisation. A clearer picture of the state of affairs may be gained by postulating the formation of hydrogen bonds between the oxygen atoms of the ionised hydroxyl groups, and all the hydrogen atoms in the organic radical. Which of the hydrogens then to be eliminated to form a permanent union with the hydroxyl ion as water will depend on which hydrogen can be lost with the least input of energy to cause the break from the organic residue. Clearly, this will generally result in loss of the β-hydrogen, for such a fragment with a lone pair of electrons on the β-carbon atom, and an open sextet on the α, can very easily stabilize itself, as has already been pointed out, merely by the shift of the lone pair of electrons to form an ethylenic link. Of course, in the event of a choice between two β-hydrogens, then the one most loosely held, as determined by Ingold's concepts, will be the one most readily eliminated. Ingold's own arguments for ruling out α elimination apply equally well here; as for γ and δ elimination, if either of these occurred, the system could stabilize itself either by a shift of hydrogen or by the formation of a three or a four membered ring. In the case of the special type of compound:

$$C_6H_5CH_2C(COOC_2H_5)_2CH_2CH_2N(CH_3)_3OC_2H_5$$

Ingold and Rogers (147a) have shown that the carbethoxyl group in the γ position undergoes elimination. Then instead of a cyclopropane ring being formed, a shift of hydrogen from the β to the α position occurs, with consequent formation of an ethylenic link in the β - γ position. Examples of the more usual ring closure on γ elimination are shown in the formation of ethylene oxides in the decomposition of ephedrine and similar compounds (p.55) and in the occurrence of tricyclene from methylbornylxanthate (p.72). A possible example of δ elimination accompanied by ring closure is to be found in v.Braun's synthesis of pirylene (147b), outlined on page 63.



The temperature of the decomposition may well bring about a

(147a) Ingold, C.K., Rogers, M.A.T. J. Chem. Soc. <u>1935</u> 722-725.

(147b) v.Braun, J., Teuffert, W. Ber.<u>61B</u> 1092-99 (1928).

rearrangement of the allene system of bonds to produce a conjugated system (cf. Schmitt and Boord (148)); then by loss of the δ hydrogen as a proton and rupture of the C-N bond, a fragment is left which undergoes ring closure to give the cyclobutene derivative. It should be pointed out however, that v.Braun's evidence for the cyclobutene structure of pirylene is not very conclusive and although he favours the 4-membered ring, the product obtained may possibly be a cyclopropane derivative formed by γ elimination of hydrogen accompanied by ring closing. Existing views on elimination and methathetical reactions in general, and the electronic theory of rearrangements have recently been discussed in a lengthy paper by Hauser (147c).

By assuming the formation of hydrogen bonds between hydroxyl groups and all the hydrogen atoms of the organic radical, as we have proposed doing, one arrives at a very satisfactory explanation of the effect of glycerol on the course of the

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(148) Schmitt, C.G., Boord, C.E. J. Amer. Chem. Soc. 54 751-61 (753) (1932).

(147c) Hauser, C.R. J. Amer. Chem. Soc. 62 933-941 (1940).

decomposition; for the glycerol, by forming relatively stable hydrogen bonds between its own hydroxyl groups and the ionised ones from the ammonium base - in effect, hydrating the ions, - prevents their access to, and formation of bonds with, the hydrogens of the organic residue. This prerequisite for the formation of water (and hence of olefin) being thus hindered., the other decomposition, going on simultaneously, yields relatively larger amounts of methyl alcohol and mixed tertiary amine. In the same way, the potassium hydroxide by providing an excess of ionised hydroxyl ions, increases the amount of hydrogen bonding that can be effective in the production of water, and hence of olefin.

The compound we have chosen with which to study the mechanism of the reaction is the quaternary base from pinacolyl amine, and it seems admirably suited for the purpose in view. Unlike the terpenes, all the isomeric hydrocarbons of the hexane series are well known and can be easily separated by fractional distillation. If the reaction proceeds by Ingold's mechanism only the unrearranged tert.-butylethylene should be evolved; if it proceeds first by rupture of the C-N bond, and then proton elimination, the same mixture of hydrocarbons as Whitmore obtained in the dehydration of pinacolyl alcohol should result; if there is a free radical involved, there should be formed 2,3-ditert.-butylbutane through simple coupling, and tert.-butylethane and trimethylcyclopropane through disproportionation. These are the same type of products as Whitmore and co-workers (149) have recently reported from a reaction known to involve free radicals. They treated neopentyl chloride with sodium, and obtained 13% yield of 2,2,5,5-tetramethylhexane, 36% yield of neopentane and 25% yield of 1,1 dimethylcyclopropane.

Keeping these various possibilities in mind the decomposition of trimethylpinacolylammonium hydroxide, was carried out at a high temperature (up to 160°C.) and also at room temperature. The basic portions of the distillate were removed as their water soluble hydrochlorides; the hydrocarbon part was separated, dried carefully over powdered potassium hydroxide, and fractionally distilled through a three foot column, packed with single turn glass helicies. By measuring the amount of N,N-dimethylpinacolyl amine, (produced by decomposition according to equation B), and of trimethylamine (produced according to equation A), the relative amount of decomposition in the two directions was calculated, and found to be approximately 50% in both ways. At room temperature on the other hand, the reaction proceeded exclusively according to reaction A - there being not the slightest trace of N,N-dimethylpinacolyl amine in the basic portions of the distillate in this case. This behaviour indicates that the velocity of reactionsA and B, which are to be considered as proceeding

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(149) Whitmore, F.C., Popkin, A.H., Pfister,J.R., J. Amer. Chem. Soc. <u>61</u> 1616-17(1939).

simultaneously, have different temperature coefficients and that whereas B is immeasureably slow at 25°, at 150° it accounts for 50% of the products of the decomposition. A second factor also of some possible influence on the decomposition is that increase of the kinetic energy of the molecule at high temperature may decrease the amount of hydrogen bonding, and thereby decrease the amount of decomposition according to A.

In preparing the olefin portion of both decompositions for distillation, great care was taken to avoid its contact with concentrated solutions of strong acids, and in the case of the decomposition at room temperature, at no time was the hydroxide, (and hence, the olefin) subjected to temperatures higher than 30°C. at the very maximum. Thus the possibility of rearrangement either by strong acids or by heat was avoided. The value, and constancy of the boiling point and refractive index of the various fractions obtained in the distillation of both olefin portions, furnished conclusive evidence that the olefin was tert.-butylethylene, with no rearranged products present. The efficiency of the column in separating mixtures of olefins had previously been tested by dehydrating pinacolyl alcohol with oxalic acid, and fractionating the resulting mixture of rearranged olefins into two components (p 138).

The following table shows the constants of the various fractions obtained in the distillation of the olefin produced in the high temperature decomposition.

	B.P. in °C.(760 mms.)(corr.)	n_D^{20}
Olefin before fractionation		1.3772
First fraction	40.3	1.3769
Second fraction	40.6	1.3769
Third fraction	40.6	1.3767
Residue		1.3790

The second table shows some previously recorded boiling points and refractive indices of tert.-butylethylene.

Author	B.P. in °C.	n_D^{20}
Fomin and Sochanski (149a)	41.2_{760}	1.37667
Schurmann and Boord (149b)	$41.0\text{-}41.2_{760}$	1.3759
Laughlin and Whitmore (149c)	$40.2\text{-}40.25_{741}$	1.3760
Dolliver et al (149d)	41.1_{760}	1.3765

The distillation of the olefin from the room temperature decomposition was carried out even more carefully, and was continued to the last 0.1 cc. of liquid. The results

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(149a) Fomin, V., Sochanski, N. Ber. 46 244-8 (1913).
(149b) Schurman, I., Boord, C.E. J. Amer. Chem. Soc. 55 4930-4935 (1933).
(149c) Laughlin, K.C., Nash, C.W., Whitmore, F.C. J. Amer. Chem. Soc. 56 1395-6 (1934).
(149d) Dolliver, M.A., Gresham, T.L., Kistiakowsky, G.B., Vaughan, W.E. J. Amer. Chem. Soc. 59 p.831-841 (833) (1937).

in this case are summarized in the following table.

	B.P. in °C.(761 mms.) (corr.) *	n_D^{20}
1st. fraction (through column)	41.1	1.3762
2nd " " "	41.1	1.3762
3rd " " "	41.1	1.3763
4th " " "	41.1	1.3762
5th " " "	41.1	1.3763
6th " (from ordinary distilling flask)	41.3-41.5	1.3762
residue (0.1 cc.)		1.3822

Even supposing the rise in refractive index of the last 0.1 cc. of olefin to be due to the presence of the rearranged hydrocarbons in the proportion in which they occur in the dehydration of pinacolyl alcohol, then it can be shown, by plotting refractive index against percent of various components in the mixture, that not more than 0.1% of rearrangement can have occurred. The absence of rearrangement at room temperature where, presumably, the decomposition is proceeding at a slower rate, is evidence against the view that failure to obtain rearranged products at high temperature is due to the speed at which the decomposition reaction occurs, and which is too rapid to permit of rearrangement taking place.

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* The author wishes to thank Mr. R.B.Harvey for standardization of the thermometer used in this distillation against a platinium resistance thermometer.

Thus the tert.-butylethylene produced in this decomposition, which can scarcely be called a "thermal" one, is of an exceedingly high degree of purity. Moreover, the boiling point data in the last table, indicates that no measurable amount of any 1,1,2-trimethylcyclopropane (b.p.56-7°), 2,3 ditert.-butylbutane-2 or tert.-butylethane (b.p.49.7°) - all higher boiling and all products to be expected if any of the alternative mechanisms outlined above had been operating.

Since from the decomposition of the quaternary base of pinacolyl amine, which presents such a good opportunity for rearrangement to occur if that is at all possible, only tert.-butylethylene was obtained, the conclusion may be drawn that the mechanism governing the reaction is one not permitting rearrangement to take place. That is to say, Ingold's view of the situation, in which a proton is expelled first (in just what manner does not immediately concern us here) followed afterwards by a rupture of the carbon - nitrogen bond seems to be the most plausible conception of the reaction. This view renders untenable the suggestion recently advanced by Ismailski and Popoff (150) that the decomposition proceeds through the intermediate formation of a radical with two free valences.

If, with the premise in mind that rearrangement does not occur on decomposition of quaternary bases,

(150) Ismailski, V.A., Popoff, B.V., Bull. Soc. Chim. [5] 3 2028-37 (2033) (1936).

we examine the reported cases of abnormal behaviour, it will be found there is no definite evidence to support the claim that rearrangement has occurred. In Shriner and Sutherland's paper (150a) for instance, they state that l-bornylene prepared from pyrolysis of trimethylbornylammonium hydroxides is contaminated with d-camphene. The only evidence presented to support this belief is that the optical rotation of the bornylene so obtained was not as high as had previously been obtained by Henderson and Caw (151), for a sample prepared in another way; Shriner and Sutherland presumably attributed the lower laevo value for bornylene to the presence of a small amount of dextro rotatory camphene - none of which was reported as having been isolated. It can not be denied that camphene may quite possibly occur, but not in the optically active form. Applying our conception of hydrogen bonding to bornyltrimethylammonium hydroxide, it will be seen that loss of the β hydrogen would yield bornylene; another possibility however, is that from some of the molecules a γ-hydrogen might be lost - and a consideration of atomic models shows clearly how close the α and γ position are to each other. Under such circumstances, the opportunity for ring formation occurs, and tricylene is produced. Now although tricylene is a fairly stable hydro-

(150a) Shriner, R.L., Sutherland, H. J. Amer. Chem. Soc. 60 1314-20 (1938).

(151) Henderson, C.G., Caw, W. J. Chem. Soc. 101 1416-20 (1912).

carbon, there are conditions whereby it may be transformed to camphene - as for instance passage over a nickel catalyst at 180 - 200° in a current of nitrogen (152). It is not inconceivable therefore that under the high temperatures required for the decomposition, a small amount of the tricylene (which occurs in quite appreciable quantities) might undergo ring opening to yield camphene. Since tricylene is inactive, the camphene so produced should be the racemic mixture, and not just the d-form. The experimental difficulties involved in a separation of the camphene from bornylene are very great, and neither Shiner and Sutherland, nor Chugaev and Budrick (153) who had reported only the formation of tricylene with the bornylene, were able to prepare an absolutely homogeneous sample of bornylene. Consequently, there is no definite evidence in the literature from which one may know whether the camphene so produced is optically active or is the racemic mixture. The point is obviously one of some importance, for if the camphene should be optically active, then tricylene can not be an intermediate, and the only alternative way by which camphene could have been produced is through a Wagner-Meerwein rearrangement; this mechanism would yield an optically active camphene, and would involve a true skeletal rearrangement.

Besides the examples of hydrogen shifts and opening

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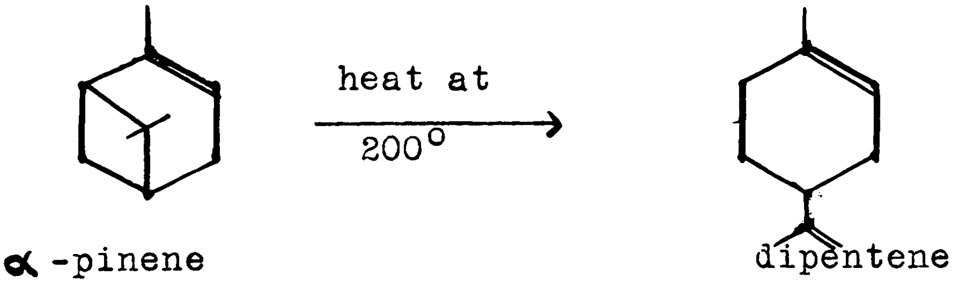
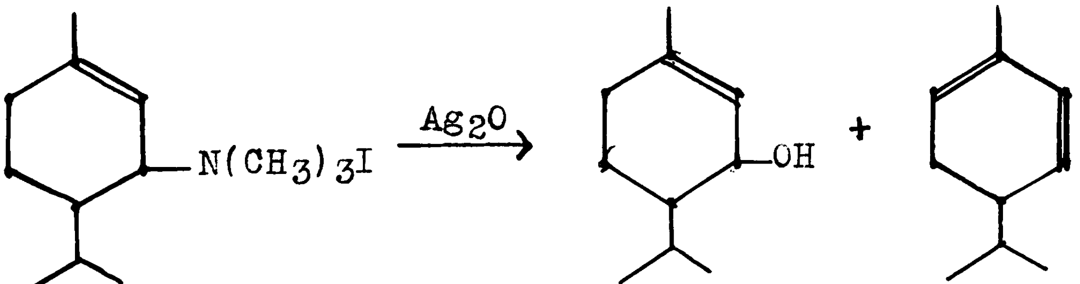
(152) Meerwein, H., v.Emster, K. Ber. <u>53B</u> 1815-29 (1920).
(153) Chugaev, L., Budrick, V. Ann. 388 280-93 (1912).

of cyclopropane rings in tricyclic compounds to be considered later, another instance of ring opening was observed by Conant and Carlson (154). They found that by heating at 200°, α-pinene could be converted almost quantitatively to dipentene. Though the ring here was a 4 membered one and not a 3, still the same shift of hydrogen was involved, with production of a second ethylenic link.



Read and Storey (155) have made the rather curious observation that distillation of l-piperityltrimethylammonium iodide with silver oxide produced, besides the almost completely configurationally inverted piperitol, the terpene α-phellandrene, with none of the expected Δ^4 -carene or α-terpinene.



However, since Read and Walker (156) also observed that the

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(154) Conant, J.B., Carlson, G.H., J. Amer. Chem. Soc., <u>51</u> 3464-69 (1929).

(155) Read, J., Storey, R.A., J. Chem. Soc. <u>1930</u> 2770-83.

(156) Read, J., Walker, J., J. Chem. Soc., <u>1934</u> 308-313.

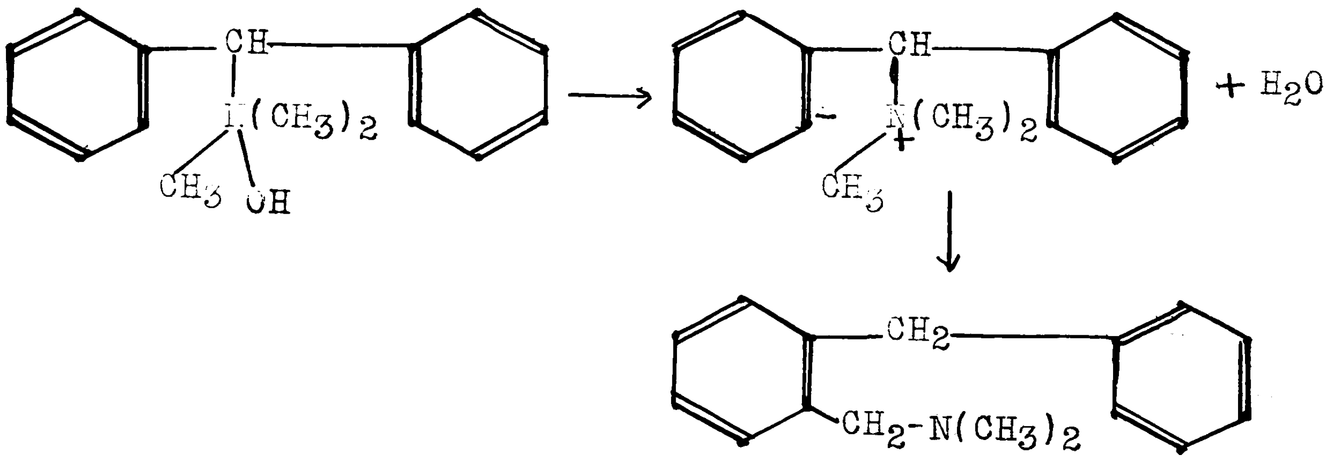
piperitol so produced, spontaneously lost water with the production of α-phellandrene and since in any case, such a shift of bonds is not a skeletal rearrangement, the observation in no way invalidates the argument in favour of a non-rearrangement mechanism for the decomposition of quaternary ammonium hydroxides. The most interesting point in the work is the production of the "higher alcohol" piperitol, instead of methyl alcohol, which can only be attributed to a looser attachment of the piperityl - nitrogen link, than of the methyl group - nitrogen bond.

In cases where elimination of the β - or γ hydrogen atom becomes hindered through configurational or other influences, the reaction may still proceed with olefin production, by elimination of the α hydrogen. Examples of this type are encountered with the quaternary base from 9-fluoryl amine (157) and from benzhydrylamine (158)(159). In the former case, the powerful forces of aromatic stability (i.e. resonance energy) might be expected to have caused the retention of the shared electrons by the carbon, in the rupture of the C-N bond. From the anion, with an open sextet so produced, one would expect the formation of fluorene on the one hand, and an amine

(157) Ingold, C.K., Jessop. J.A., J. Chem. Soc. 1929 2357-61.
(158) Hughes, E.D., Ingold, C.K., J. Chem. Soc. 1933 69-75.
(159) Stevens, T.S., Creighton, E.M., Gordon, A.B., MacNicol, M., J. Chem. Soc., 1928 3193-97.
Stevens, T.S., J. Chem. Soc. 1930 2107-2119.
Stevens, T.S., Snedden, W.W., Stiller, E.T., Thomson, T., J. Chem. Soc. 1930 2119-25.

oxide on the other. Since no trace of either of these were found, it follows that the decomposition must proceed through α-elimination; this process, with the accompanying rupture of the C-N bond yielded a di-valent radicle which combined with a second one to produce difluorylidene.

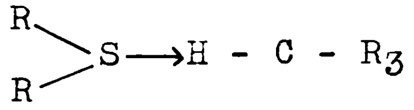
The case of benzhydrylamine is less clear owing to the uncertainty as to the structure of the rearranged product. If, as Ingold thinks, the product is N,N-dimethyl-1,1-diphenylethylamine $(C_6H_5)_2C\,CH_3.N(CH_3)_2$ then its presence can be explained by assuming elimination of the α hydrogen, but with no rupture of the C-N bond taking place. The dipole $\{(C_6H_5)_2\overset{-}{C}.\overset{+}{N}(CH_3)_3\}$ so formed can then stabilize itself through shift of a methyl group (without its shared electrons) from nitrogen to carbon.(159) Should the rearranged product be N,N dimethyl-o-benzylbenzylamine as Sommelet claims he obtained, then the decomposition of the quaternary base would seem to involve, as the first step, the elimination of a γ-hydrogen atom, followed by a very complex molecular rearrangement, resulting finally, in attachment of the nitrogen through one of its former methyl groups, to the ortho position in the benzene ring, rupture of the original benzhydryl-nitrogen link, and addition of a proton to compensate for the loss of nitrogen.



Since there is no evidence to show that tricyclene is not an intermediate in camphene formation in the decomposition of bornyltrimethylammonium hydroxide, trimethylbenzhydrylammonium hydroxide then remains the outstanding example of a quaternary ammonium base that yields on decomposition, an apparently rearranged product. Even here, however, there is some uncertainty as to the actual structure of the product obtained, either possibility involving a most remarkable rearrangement. The one required by Ingold to account for his product seems to be the more straightforward of the two, but such shifts of methyl groups, without their shared electron pair are certainly uncommon, even though reported by Stevens and co-workers (159). With this possible exception then, there have been no other cases observed of skeletal rearrangement in such decompositions, and every case conforms to our modification of Ingold's theory.

Considering with what success the concept of hydrogen bonding may be applied in the quaternary ammonium hydroxide series, it has seemed to us that somewhat similar principles should apply in the decompositions of various esters to produce unrearranged olefins- a reaction for which no general mechanism has hitherto been proposed. The probability that closely analogous mechanisms govern both reactions is increased by virtue of the fact that these two elimination reactions resemble each other, and differ from the majority of such eliminations in the freedom from rearrangement of the evolved hydrocarbons.

As in the decomposition of quaternary bases, so in the xanthate and other esters, olefin production apparently proceeds through expulsion of a β- hydrogen atom, accompanied by rupture of the carbon - oxygen bond. The β- hydrogen is generally the one to be eliminated, not because of any increased activity of this hydrogen over any other in the molecule, but because the system produced by loss of this hydrogen and rupture of the carbon - oxygen bond can become stabilized through the shift of one pair of electrons to produce an ethylenic bond, with the least energy change. If, through absence of a β- hydrogen, or because of its non-availability as a result of electronic influences of neighboring groups, a γ- hydrogen may then be expelled instead, with consequent possibility of ring formation. Continuing the analogy with the quaternary hydroxides it seems that the most likely initial factor in promoting the elimination of hydrogen is, in the case of the xanthates, the formation of a sulphur-hydrogen bond, between the doubly bound sulphur of the xanthate group, and near-by hydrogen atoms in the organic portion of the molecule. It has been commonly supposed that hydrogen bonding was restricted to hydrogen atoms attached to fluorine, oxygen or nitrogen (160) but the recent work of Marvel and his school (160)(161) and by other workers (161a) has suggested that hydrogen bonding is more common than hitherto believed, and moreover, will occur between a hydrogen attached to another atom by a sufficiently ionic link and a second (donor) atom containing an unshared pair of electrons. While there is only a very weak hydrogen bond between hydrogen and sulphur in a thio-ether link,



there is no direct evidence to show whether or not a very stable hydrogen bond of the type $R_2C{=}S \longrightarrow H\text{-}C\text{-}R_3$ can exist between hydrogen and sulphur in a thio-ketone link. However, it is quite probable that a more stable hydrogen bond could exist with this group, and in any case, the mere tendency towards orientation in this direction might be sufficient to

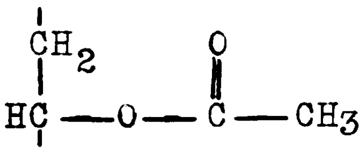
(160) Copley, M.J., Marvel, C.S., Ginsberg, E., J. Amer. Chem. Soc. <u>61</u> 3161-2 (1939).

(161) Copley, M.J., Zellhoefer, G.F., Marvel, C.S. J. Amer. Chem. Soc. 61 3500-2 (1939).

(161a) Gordy, W., Stanford, S.C. J. Amer. Chem. Soc. <u>62</u> 497-505 (1940).

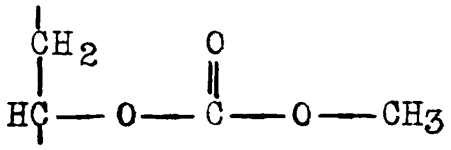
determine the course of the reaction; under the influence of the high temperature required for the decomposition the effect would be enough to promote the formation of a true C - S - H bond, with simultaneous rupture of the original H - C bond.

In the xanthate ester of course, there are two sulphur atoms, either one of which might be regarded as forming the required sulphur-hydrogen bond; however, the atom most likely to form such a bond would seem to be the one in the thio-carbonyl link. This conclusion is drawn as a result of the apparently greater stability of analogous esters - the acetates (162) and organic carbonates. These three classes may be represented graphically as follows:



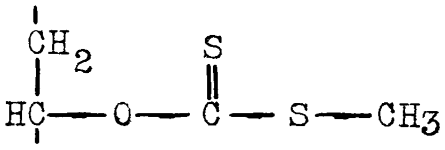
$$\overset{\overset{|}{CH_2}}{\overset{|}{\underset{|}{HC}}}-O-\overset{O}{\overset{\|}{C}}-CH_3$$

acetate



$$\overset{\overset{|}{CH_2}}{\overset{|}{\underset{|}{HC}}}-O-\overset{O}{\overset{\|}{C}}-O-CH_3$$

carbonate



$$\overset{\overset{|}{CH_2}}{\overset{|}{\underset{|}{HC}}}-O-\overset{S}{\overset{\|}{C}}-S-CH_3$$

xanthate

Little is known of the pyrolysis of simple alkyl or aryl carbonates (163), but from the fact that many are reported as boiling at quite elevated temperatures with no decomposition, it appears that they decompose less readily than do the xanthates. If in the carbonates, it were the ether-linked oxygen - which ordinarily forms a hydrogen bond quite readily - that in this case bonded with the β hydrogen, then these compounds would be expected to decompose more easily than the xanthates; this

(162) Wibaut, J.P., Van Pelt, Jr. A.L., Rec. trav. chim., 57 1055-58 (1938).

(163) Hurd, C.D. The Pyrolysis of Carbon Compounds, Chemical Catalogue Co., (1929) p 545.
Beilstein, 4th Ed. 3 4-7 (1921).

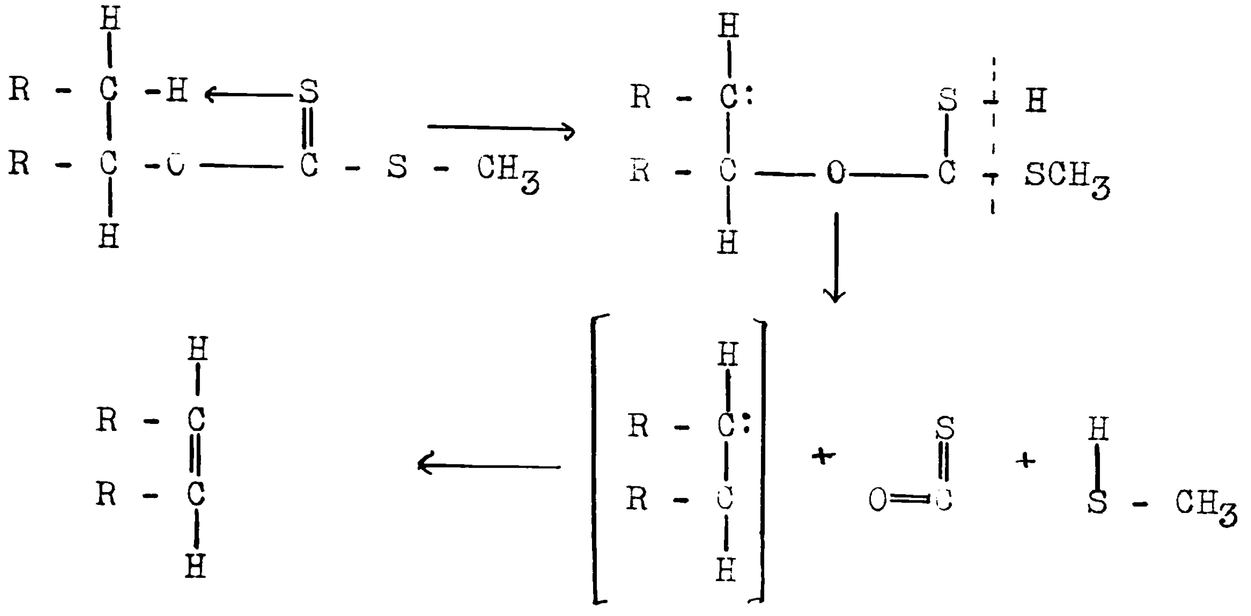
assumption requires about equal stabilities for the two carbon-oxygen links between the organic portion itself and the functional group, and is in accord with the knowledge that hydrogen bonding in R - S - R compounds is very slight (160). But since a lesser stability compared with the xanthates is not observed, one concludes that the hydrogen bond forms with the doubly bound oxygen. The lesser stability of the xanthates is then explained as being due, in part at least, to a somewhat firmer bond between doubly bound sulphur and hydrogen, than between doubly bound oxygen and hydrogen.

One could reasonably expect a greater reactivity on the part of the thio-ketone link than of the ketone itself, considering the well-known, peculiar reactivity of the $C{=}S$ linkage (164). This, for instance, is responsible for the fact that thioacetone, and even thioacetophenone polymerise so readily that the former, at least, is known only in the trimeric form; acetone, on the other hand, is quite stable as the monomer. Compounds with less active thiocarbonyl groups, corresponding to esters, acid chlorides and lactones are monomeric, but some of them, such as thiophosgene readily polymerise, in contrast to phosgene itself.

The product formed by actual transfer of β-hydrogen to doubly bound sulphur is a thio acetal, which can be considered as undergoing the usual cleavage of acetals to give here, a thio alcohol, methyl mercaptan. The steps of the reaction

(164) Whitmore, F.C. Organic Chemistry, D. Van Nostrand Co. 1937 p.253.

are then represented as follows:



Again, as in the quaternary ammonium hydroxides, the preliminary removal of a proton has left available a lone pair of electrons. Upon subsequent breaking of the C-O bond (the oxygen retaining the pair of shared electrons) the system stabilizes itself merely by shift of the lone pair of electrons, and an ethylene link is produced. This process goes on with so little energy change that there is no tendency for the more difficult process, shift of a complete group, with its pair of shared electrons, to occur.

As a supplement to these theoretical considerations, an inspection of molecular models of various substances dehydrated by the xanthate method has shown that in every case, it is sterically possible to form hydrogen-sulphur bonds, which on decomposition in the manner outlined above would yield any of the observed products. For instance, the molecular model of methylbornylxanthate shows a favourable steric configuration for the formation of a bond between sulphur and the β hydrogen atom - and this on decomposition, would yield bornylene. With almost equal ease, a bond could form with the γ hydrogen, to produce on decomposition, a fragment with the electronic requirements for ring closure - and tricyclene would be obtained. There is, of course, in bornylene, a second β - hydrogen atom, with which hydrogen-sulphur bonding is possible, the one at the junction of the bicyclic ring system, but according to Bredt's rule such an elimination would not occur, owing to the impossibility of producing a compound with an ethylenic bond at the bridge head.

In order to obtain some experimental evidence to support the view that any hydrogen atom, sterically capable of forming a hydrogen bond with either sulphur atom in the xanthate, should be eliminated to a greater or less extent, the decomposition of several xanthate esters has been investigated. The first one to be studied was that of the monoxanthate ester of 2,3-butylene glycol. It was found, as expected in the light of Fomin's work on the monoxanthate of pinacol (165) that the chief product was formed through elimination of the hydrogen from the adjacent hydroxyl group - actually the one in the γ - position. In this particular case, the fragment formed by transfer of hydrogen from oxygen

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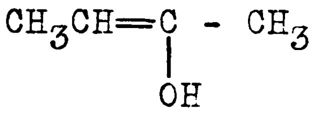
(165) Fomin, V., J. Gen. Chem. (U.S.S.R.) 5 1192-4 (1935).

to sulphur, was then capable of attaining a stable configuration, merely by loss of methyl mercaptan, without carbon oxysulphide being formed as well.

In addition to this cyclic thio-carbonate, there also appeared a product resulting from loss of the secondary β -hydrogen (as contrasted with the primary hydrogen, forming part of the terminal methyl group, and also in the β - position to the xanthate group). This substance was methyl ethyl ketone - the keto form of enol:

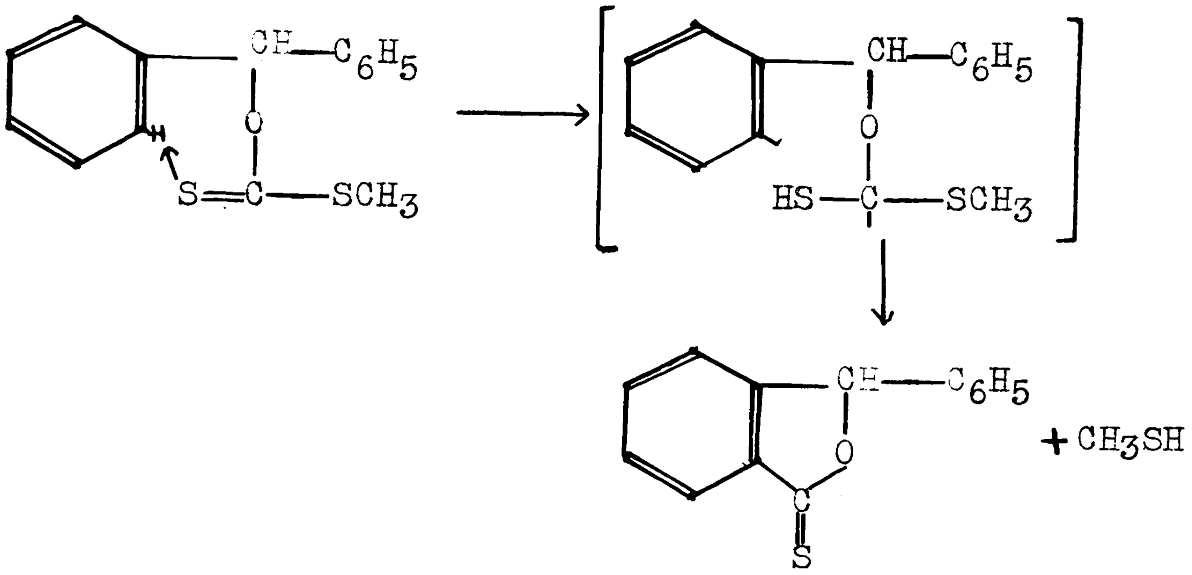


$$CH_3CH{=}\underset{\displaystyle OH}{\underset{|}{C}} - CH_3$$

Owing to the instability of four-membered rings, there is no tendency here (nor in any β - elimination) for retention of the -O-C-S portion of the molecule in a cyclic compound, as was encountered in this same substance, with γ - elimination.

Some time ago, the dehydration of benzhydrol by the xanthate method had been reported (166), and the only product recorded as being isolated was tetraphenylethylene. Benzhydrol however, is a substance in which a hydrogen-bond might easily be formed between the sulphur, and the hydrogen in the γ - position to the point of attachment of the xanthate group - i.e.- the ortho position in the benzene ring. If loss of hydrogen as methyl mercaptan occurred in the manner postulated above, one could anticipate the formation of a new thio-lactone type of ring system in the compound.

(166) Kursanoff, D. J. Russ. Phys-Chem. Soc. Chem. Part 60 No. 6 921-4 (1928).



Such a cyclic compound, on hydrolysis with sodium hydroxide should yield the lactone of o-(α - hydroxybenzyl) - benzoic acid. It therefore seemed of interest to reinvestigate the decomposition, to find whether this expected product was obtained. After long boiling of the residue from the decomposition of the methylxanthate ester of benzhydrol, filtration to remove the insoluble material, and acidification of the filtrate, there was obtained a very small amount of a rather tarry solid, which we were unable up to the present time, to identify. Its acidic nature was shown by its solubility in aqueous sodium carbonate, from which it could be precipitated upon addition of acid. If this is the lactone, oxidation should yield o-benzoylbenzoic acid; its solubility in carbonate solution however, would seem to render this possibility rather unlikely,

The main products of the decomposition however, proved to be of considerable interest. Contrary to Kursanoff's work, we were unable to find any tetraphenylethylene, isolating instead, tetraphenylethane, in 30% yield - and diphenylmethane in 58% yield - the latter compound apparently not observed at all by Kursanoff. The production of tetraphenylethane recalls the manner of decomposition of benzhydrol (166a) itself, and which gives, in addition, benzophenone and diphenylmethane - these compounds occurring through intermediate formation of dibenzhydrylether. In the case of the xanthate decomposition, the formation of benzophenone was not observed, and accordingly it would appear that this was not an oxidation and reduction reaction, nor does it likely involve the same mechanism as governs the decomposition of benzhydrol itself. The formation of diphenylmethane and tetraphenylethane would seem to indicate the presence of the free radical $(C_6H_5)_2CH-$. This fragment could either couple with a second to produce tetraphenylethane, or in the presence of other xanthate decomposition products, it could capture a hydrogen atom to produce diphenylmethane. It is admittedly odd that no disproportionation should occur, to yield tetraphenylethylene and diphenylmethane. Moreover, the failure to produce the former compound would seem to indicate that this cannot be a case of α elimination, with

(166a) Nef J.U. Ann. <u>298</u> 202-374 (233,236) (1897).

the formation of the fragment $(C_6H_5)_2C=$. For it is unlikely that were this to be formed it should take up either one atom of hydrogen, and couple to produce tetraphenylethane, or two atoms to yield diphenylmethane, all to occur before it coupled immediately to the ethylenic compound. The occurrence of tetraphenylethane produced here, virtually in the absence of oxygen, is in accord with the properties of the diphenylmethyl radical as reported by Nauta and Mulder (166b) and who found that by excluding oxygen from the reaction, diphenylmethylchloride and silver gave a quantitative yield of tetraphenylethane.

As to the question of rearrangements in dehydration by the xanthate method, the adoption of the mechanism we have proposed for the reaction makes it very difficult to account for any truly rearranged products. As in the case of quaternary ammonium hydroxide, there does not seem to exist in the literature any incontrovertible piece of evidence to show that rearrangement has occurred in a xanthate dehydration. The only cases in which circumstantial evidence might indicate rearrangement are in the terpene series, where superimposed effects, the result of the peculiar steric configuration of these compounds comes into play, and renders them very susceptible to effects of high temperature. In the aliphatic series, where the various products of dehydration, whether normal or rearranged, - are more stable to heat - there is

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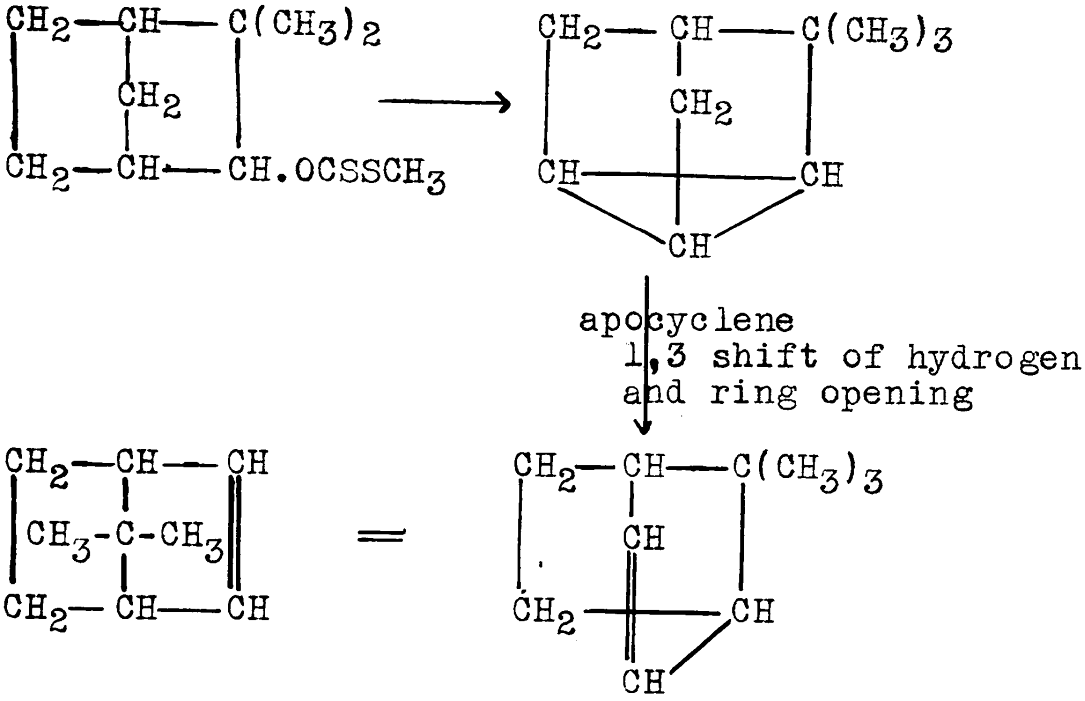
(166b). Nauta, W.Th., Mulder, D. Rec. trav. chim. <u>58</u> 1070-80 (1939).

ample evidence to show that even from such easily rearranged compounds as pinacolyl alcohol, absolutely none of the abnormal product is obtained.

Possibly the most outstanding apparent case of xanthate dehydration said to involve a Wagner rearrangement was Komppa's (167) observation of the occurrence of apobornylene, together with apocyclene in the pyrolysis of methylcamphenilylxanthate. However in the absence of any direct evidence as to whether or not apocyclene is stable under the conditions of the experiment (the temperature of the decomposition was not recorded, but it must have been considerably above 152-155° - at which range the xanthate ester distilled unchanged at 10 mms. pressure) and since apocyclene is the major product of the reaction, it seems not unreasonable to suppose the latter is an intermediate in the formation of apobornylene. The bicyclic compound by a 1,3 shift of hydrogen, with rupture of the cyclopropane ring, could be transformed to any one of a variety of products, depending on which hydrogen shifted, and in which way the ring opened. The steps in apobornylene formation may then be represented as follows, and it will be noted that they involve no structural rearrangement.

(167) Komppa, G., Roschier, R.H. Ann. 429 175-190 (1922).

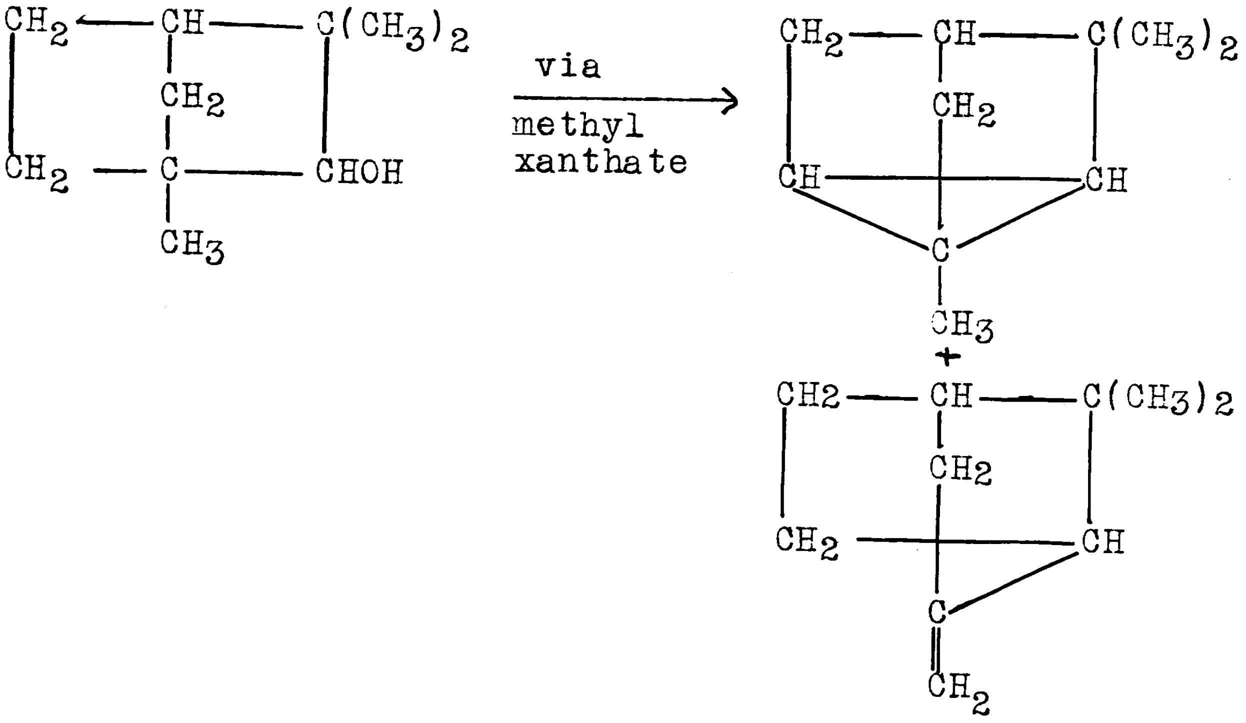


apobornylene

This is exactly similar to the alleged formation of camphene from bornyltrimethylammonium hydroxide, and of camphene from methylbornylxanthate, which as has been shown, probably proceed through the intermediate tricyclene. McAlpine (168) was apparently of the opinion that the camphene obtained with bornylene from the decomposition of methylbornylxanthate was optically active, but the evidence for this belief was not particularly conclusive, and was not based on any separation of the two components, with actual measurement of the activity, if any, of the camphene.

Another xanthate decomposition apparently involving rearrangement, is the production of α-fenchene together with cyclofenchene in the dehydration of fenchyl alcohol (169).

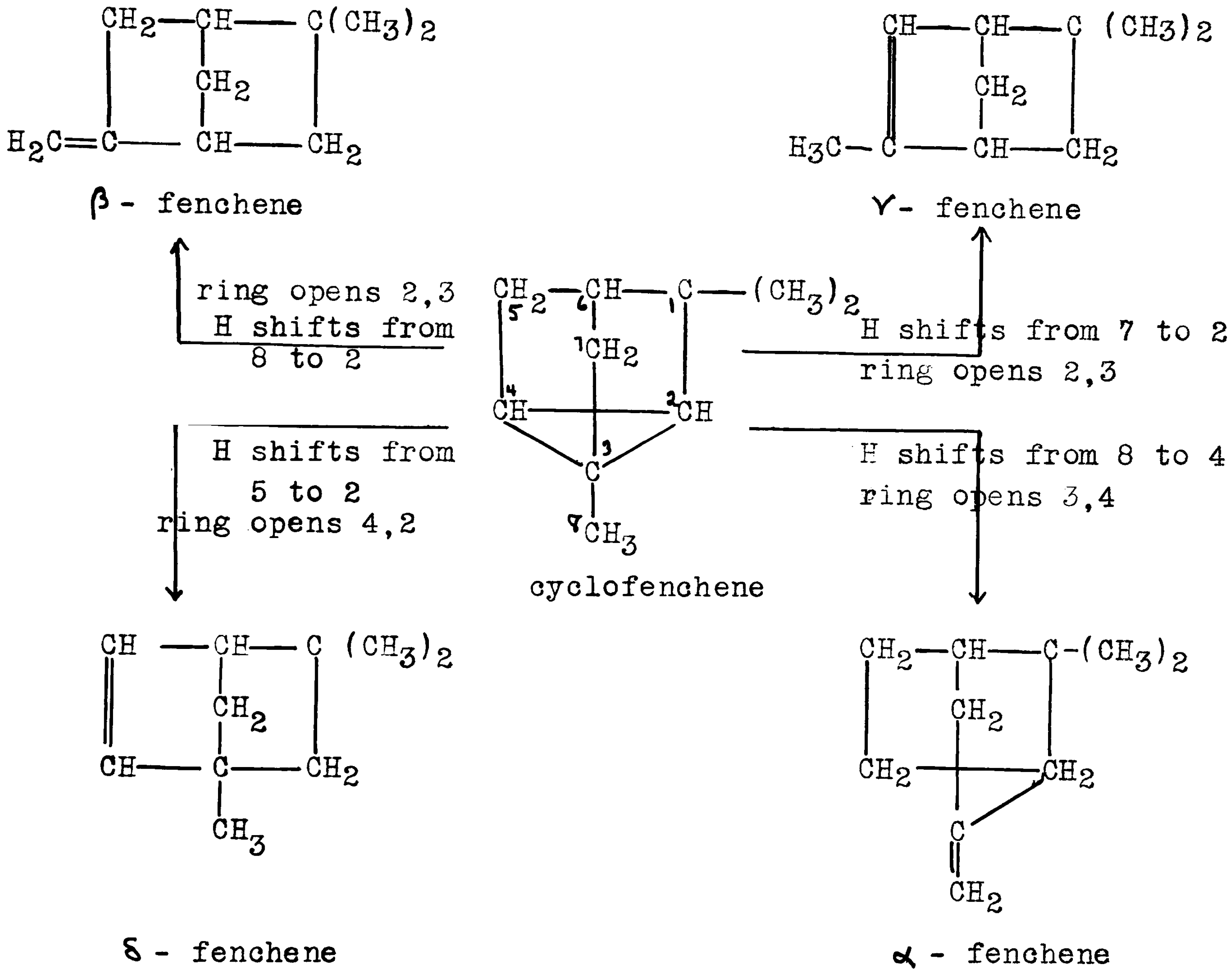
(168) McAlpine, I.M. J. Chem. Soc. 1931 1114-21.
(169) Komppa, G., Nyman, G.A. Ann. 535 252-66 (1938).



α -fenchene

Again however, there is no valid evidence against the assumption that cyclofenchene is an intermediate in the formation of α - fenchene; contrary to the case of camphene, the α - fenchene produced here can have an optical activity, even when formed with cyclofenchene as an intermediate, for cyclofenchene unlike tricyclene is optically active.

Komppa and Nyman have definitely shown that cyclofenchene is an intermediate in the formation of β, γ and δ fenchenes. Each of these arises through a different 1,3 shift of hydrogen, accompanied by opening of the cyclopropane ring in the manner shown below:



The cyclopropane ring in cyclofenchene, and indeed as it may do in all tricyclic compounds of this type, is here acting as it frequently does in simple cyclopropane derivatives, as an ethylenic link. Thus a 1,3 shift of hydrogen is merely an allyl (prototropic)shift of the type:

$$C_6H_5CH_2\text{-}CH{=}CH_2 \qquad C_6H_5CH{=}CH\text{-}CH_3$$

It is not clear in all cases whether a hydrogen ion or a hydrogen atom is involved, but in heating cyclofenchene with potassium bisulphate, it is undoubtedly a hydrogen ion. Conant and Carlson's example of the pinene ⟶ dipentene transformation may also well be a case of hydrogen shifting with simultaneous ring opening. Now the reagent bringing about the change of cyclofenchene to β γ, and δ fenchenes is potassium bisulphate, and by its action none of the α isomer appears. On the other hand, dehydration of fenchyl alcohol by the xanthate method produces only cyclofenchene and α- fenchene - which two compounds bear the same relation to each other as do apocyclene and apobornylene, from camphenilol . Conditions must obviously be different in the two reactions i.e. - the reaction of cyclofenchene with potassium bisulphate to produce β,γ, and δ fenchenes, and the reaction of cyclofenchene formed during the decomposition of methylfenchylxanthate, to produce as we suppose it does, α - fenchene. If this were not so, the cyclofenchene in the latter case would also decompose to yield the β , γ and δ isomers, none of which was found. In other words, the β,γ and δ fenchenes come from cyclofenchene on heating in the presence of acidic reagents - in this case, potassium bisulphate, while α fenchene is produced from the same intermediate by heating with neutral reagents - here, a methylxanthate ester. As evidence for the view that different reagents might open the cyclopropane ring of cyclofenchene in different ways, there is Kohler amd Conant's (170) work on substituted cyclopropanes,

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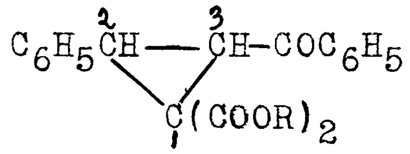
(170) Kohler, E.P., Conant, J.B. J. Amer. Chem. Soc. 39 1404-20 (1917).

in which they showed that in compounds of the type



basic reagents like alcoholates, ammonia and amines opened the ring in the 1,2 position; nascent hydrogen effected reduction and gave a product resulting from ring opening in the 1,3 position; with halogen acids in glacial acelic acid, the ring is opened in the 2,3 position.

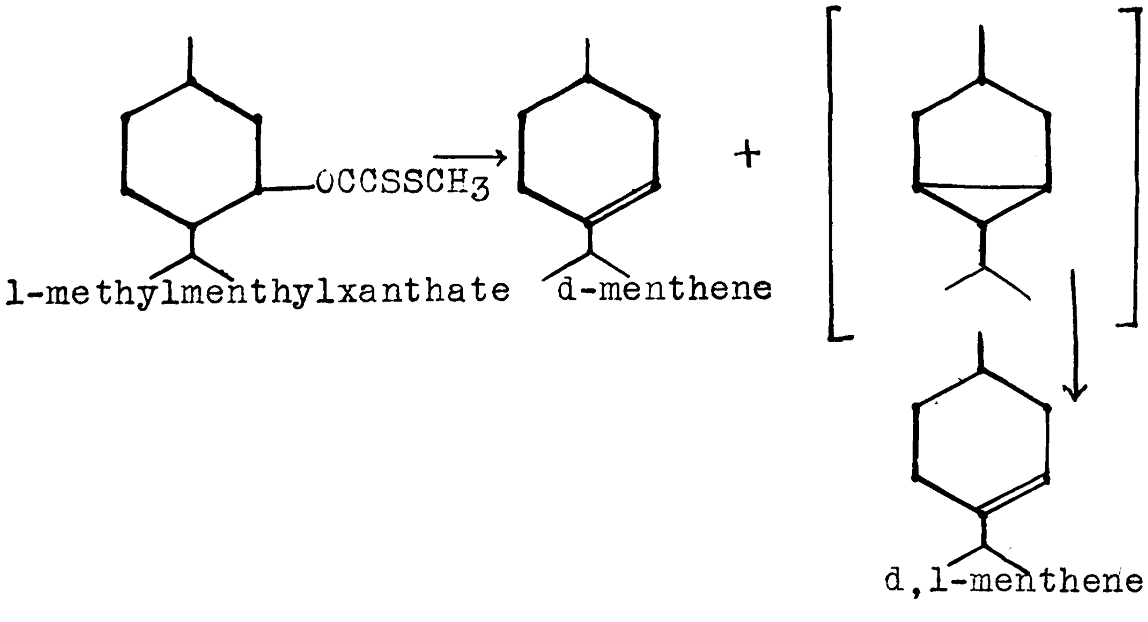
In the light of this work, it is not surprising then, that change in pH of the medium should alter the mode of ring opening and hydrogen shift in cyclofenchene, to produce on the one hand β , γ and δ isomers, and on the other, only the α isomer. Further support for the view that cyclofenchene is an intermediate in the formation of α- fenchene lies in the fact that if at any time the carbon atom holding the xanthate portion had been left with an open sextet prior to the expulsion of a proton (in the γ- position) then one would have expected the shift of a methyl group to occur from the adjacent β- carbon atom, with consequent formation of methylsantene; careful search however, by Komppa and Nyman failed to reveal the presence of this isomer in the products from xanthate dehydration of fenchyl alcohol. These authors, however, did obtain methyl santene from fenchyl alcohol when the dehydration was accomplished by phthalic anhydride or phosphoric acid. In this case, the elimination reaction undoubtedly does involve the formation of an open sextet just as in the dehydration of pinacolyl alcohol where the rearranged olefins, tetramethylethylene and unsym. - isopropylethylene are produced.

In the light of such evidence it seems reasonable to assume that olefin production, in the xanthate dehydration of terpene carbinols capable of forming a tricyclic hydrocarbon, takes place through this tricyclic form. It is significant too, that only from terpene carbinols possessing an available hydrogen, and therefore capable of forming a tricyclic form is any of the so-called rearranged olefin produced. Camphene production in the pyrolysis of methylbornylxanthate is now attributed to ring opening,under conditions of the experiment, of tricyclene, which is known to be formed with bornylene in quite large amounts.

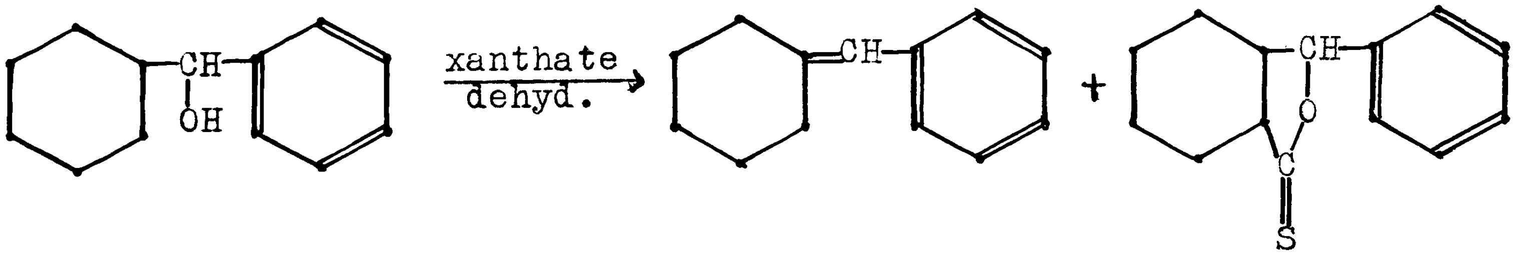
Such a mechanism of ring formation and reopening may account for the remarkable difference in optical activity of samples of menthene prepared by McAlpine (171) from methylmenthylxanthate. As has already been pointed out she observed that menthene produced by rapid decomposition at high temperatures had a greater optical rotation than samples produced by slower decomposition at lower temperatures. The effect was not one of racemisation, for menthene itself was unaffected by the experimental condition; nor did McAlpine think the

(171) McAlpine, I.M. J. Chem. Soc. <u>1932</u> 906-912 (908).

enhanced activity at high temperature was due to the "forced" formation of the Δ^2isomer, which, having one more optically active carbon atom, might be expected to have a greater optical activity. (It should be pointed out that the evidence against the formation of Δ^2- menthene was merely failure to obtain two nitrosochloride derivatives from the hydrocarbon fraction of the decomposition.) A possible explanation for this phenomenon, for which McAlpine was unable to account, is that in the slower decomposition, there is temporarily formed a bicyclic compound, which decomposed again, but being symmetrical yielded d,l menthene, and so lowered the activity of the final product.



Other substances whose dehydration by the xanthate method it is proposed to investigate are phenyltert.-butyl carbinol, and ditert.-butyl carbinol. These possess available hydrogen atoms only in the α and γ- positions and might be expected to form thio lactones analogous to that possibly produced in very small amounts in the dehydration of benzhydrol by the xanthate method. A third interesting compound already investigated by Kursanoff (172) is benzylcyclohexyl carbinol. By xanthate dehydration, he obtained a small yield of benzylidene cyclohexane and he reported the formation of quite a large amount of sulphur containing residue. This, on investigation might prove to be the lactone formed through elimination of the hydrogen of the cyclohexyl ring in the position,



However the dehydration that should definitely settle the question of mechanism of xanthate decomposition is that of isoborneol. In this compound the hydroxyl group and the bridge are on the same side of the ring, and when the hydroxyl is replaced by the xanthate group, it becomes sterically impossible to form a hydrogen-sulphur bond with the hydrogen in the γ- position due to the interference of the bridge ring; tricyclene formation is therefore rendered impossible (and hence camphene too) and the decomposition should yield pure bornylene. It is true that 4-methylborneol and 4-methyl-

(172) Kursanoff, , D. Ber. 64B 2297-2301 (2300) 1931.

isoborneol have been reported (173) to yield the same 4-methylbornylene, with no tricyclene, but unless the 4-methylborneol gave tricyclene, and the corresponding isoborneol did not, the evidence apparently supporting our theory is not conclusive. The methyl group may possibly exert some influence on the molecule which hinders tricyclene formation, even in the xanthate of 4-methylborneol.

To conclude then, this work has shown that certainly in aliphatic and alicyclic cases at least, the decomposition of quaternary ammonium hydroxides to yield an olefin proceeds with no skeletal rearrangement, and is the result of ejection of a hydrogen atom as a proton, induced through hydrogen bonding, followed by rupture of the carbon-nitrogen bond. In the case of aromatic compounds, with the peculiar electronic influences of the benzene ring the picture is slightly more complicated, but even in benzhydryl amine, owing to the uncertainty of the structures of the products obtained, the case for rearrangement can scarcely be considered to be definitely established. Decomposition of xanthates (and of esters in general) follow the same rules, and yield products free from rearrangement. As in the former case, hydrogen bonding would seem to be involved, but with this difference - that here the bonding is intramolecular, while in the ammonium hydroxides it is intermolecular.

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(173) Shavrygin, A.I., J. Gen. Chem. (U.S.S.R.) 9 516-21 (1939).

EXPERIMENTAL PART

PINACOLYL OXIME.

In a 2 litre, three necked flask fitted with a mercury sealed stirrer and a reflux condenser, were placed one hundred and ten ccs. of pinacolone, b.p. 105-6° (760 mms.), 330 ccs. of a 5.M solution of hydroxylamine hydrochloride, 330 ccs. of a 5. M solution of sodium acetate and 550 ccs. of methyl alcohol. The mixture was refluxed on the steam bath and stirred for two hours. Then it was cooled in ice and salt, the pinacolyl oxime purified by steam distillation, and dried; melting point 76°.

Subsequent runs were made, using hydroxylamine neutral sulphate in place of the hydrochloride.

REDUCTION OF PINACOLYL OXIME TO PINACOLYL AMINE.

A solution of 96 gms. of pinacolyl oxime, dried in a dessicator over sodium hydroxide, in 1670 ccs. of absolute ethyl alcohol was heated to boiling in a 5 litre flask. The flask was equipped with a 150 cm. reflux condenser, of which the inner tube was very wide (2.5 cm.). A Y tube was placed in the top of this condenser, a Friedrich condenser in one arm, a rubber stopper in the other. As soon as the alcohol began to boil, the steam was shut off and the temperature maintained by introducing strips of sodium through the free arm of the Y tube. The total amount of sodium added was 208 grams, and it was dropped in as rapidly as possible without loss of alcohol. Between periods of addition, the free arm of the Y tube was kept stoppered.

When the sodium had all dissolved, the solution was cooled and diluted with 2080 ccs. of water. The flask was then equipped with a condenser set for downward distillation, the distillate being carried below the surface of a solution of 125 ccs. of conc. HCl in 125 ccs. of water in a second five litre flask, and continued until the distillate no longer gave a basic reaction with litmus.

The alcohol, water and unreacted oxime were removed from the solution of the amine hydrochloride by distillation under reduced pressure. This was continued until the volume of the amine hydrochloride solution had been reduced to about 200 ccs. The flask with this solution was cooled and fitted with a reflux condenser, through which was added a solution of 415 ccs. of 40% potassium hydroxide. The pinacolyl amine layer was separated, dried over pellets of sodium hydroxide for 24 to 30 hours, and then distilled through a short packed column; boiling point, 103°- 104° (753 mms.), yield 75.5% n_D^{25} 1,4111.

Although the yield in this reaction was good, such large quantities of absolute alcohol had to be prepared, that other simpler methods of obtaining the amine were investigated.

The first of these was the use of aluminum isopropylate as a reducing agent, in the manner described by Lund (174). This reagent has proven to be of great value in the reduction of ketones to carbinols, but so far as we are aware, has not been tried with oximes.

In a flask fitted with a Widmer column, 10 gms. of oxime were refluxed with an excess of aluminium isopropylate in isopropyl alcohol, at such a rate as to cause a very slow distillation of the alcohol. This was continued for several hours, the distillate being tested from time to time for the presence of acetone by means of a dilute solution of 2,4-dinitro phenylhydrazine in 2 N. HCl. No trace of acetone could be detected, even after allowing the mixture to stand overnight and refluxing again the following day, and so, it was concluded that no reduction occurred.

Another attempt to reduce the oxime, following the procedure of Tseng and Chang (175), by means of amalgamated aluminium was made. Five gms. of finely powdered aluminium were amalgamated by treating with a solution of mercuric chloride. The aluminium was filtered, washed with water, then with alcohol. It was suspended in aqueous alcohol solution, 2 gms. of oxime added, and the mixture was stirred at room temperature for seven hours. No trace of the amine could be detected, and the oxime was recovered unchanged.

(174) Lund, H. Ber. <u>70B</u> 1520-5 (1937).

(175) Tseng, C. and Chang, C., Science Repts., Natl. Univ. Peking <u>1</u> No.3, 19-33 (1936). Chem.Abs. <u>31</u> 95 (1937).

The most convenient method turned out to be reduction of pinacolone with ammonium formate. This reaction between ketones and ammonium formate was discovered by Leuckart (176), and extended by Wallach (177), Freylon (178) and most recently, Ingersoll (179). The method used here however, varies somewhat from these previous cases, such as the reduction of acetophenone, camphor and the like, owing to the fact that heretofore higher boiling ketones than pinacolone have always been used.

Forty-two grams of ammonium formate were placed in a 500 cc. three necked flask, fitted with a thermometer extending to the bottom of the flask, a dropping funnel, and a modified Soxhlet extractor, carrying a reflux condenser in the top. The Soxhlet was modified by having the ordinary syphon removed, and a short piece of rubber tubing with a pinchcock, substituted. This arrangement permitted the lower layer of the distillate to be removed from the system from time to time by removing one end of the rubber tube; by replacing the rubber tube, the upper layer could be returned to the flask. Twenty-one grams of pinacolone (redistilled at 106-7°, 760 mms.) were placed in the dropping

(176) Leuckart, R. and Janssen, H. Ber. 22 1409-1413 (1413) (1889).
(177) Wallach, O., Hüttner, K., and Altenburg, J. Ann. 343 54-74 (1905).
(178) Freylon, G., Ann. chim. phys. (8) 15 140-144 (141)(1908).
(179) Organic Syntheses, John Wiley & Sons 17 76-79 (1937).

funnel, and after the ammonium formate had been heated to 125°, was added dropwise to the molten salt. Distillation into the Soxhlet begam, the pinchcock being closed. At first, most of the pinacolone that had been added distilled out of the mixture into the Soxhlet, together with water; after 10-15 ccs. of water had been drained off from the distillate, the mixture was refluxed with the pinchcock open. Less and less pinacolone distilled, until finally, none at all came up, and by this time the temperature of the mixture in the flask had risen to 175°. The heating was discontinued, the flask cooled and the contents, now homogeneous, extracted with benzene. Twenty five ccs. of conc. HCl was added to the benzene solution and the mixture refluxed for three hours. The flask was cooled, and the lower aqueous layer, containing the amine hydrochloride, separated from the benzene. The last traces of benzene, and excess water were removed by distillation under reduced pressure, until the salt was on the point of crystallizing out of solution. An excess of 30% aqueous sodium hydroxide solution was added, the free amine separated, and dried over pellets of NaOH, and distilled, B.P. (755 mm.) 103-104°. Yield, 66%. Although the yield here was somewhat lower than was obtained in the reduction of the oxime with sodium and alcohol this was off-set by the greater ease of procedure.

Later runs revealed how important it was to allow sufficient time for hydrolysis of the substituted formamide with the hydrochloric acid, and with larger quantities of materials it was found advisable to continue the refluxing for as long as six hours, to ensure complete hydrolysis.

In fractionally distilling the basic material from these larger runs, there appeared a more volatile amine, boiling point 86°at 760 mms. $n_D^{25} = 1.4142$, picrate 180°, phenylisocyanate derivative, m.p. 175°, and amounting to 5-10% of the total basic product. Attempts to identify this amine have so far proved fruitless. A survey of the literature has revealed no isomeric 6-carbon atom primary amine with this boiling point. Failure to obtain a nitroso derivative with nitrous acid eliminated the possibility of its being a secondary amine, and established its non-identity with di-isopropylamine which boils at 84°C. (179a). A 5-carbon atom amine, methylisopropylcarbinyl amine, was reported (179b) as boiling at 84-87°, and accordingly, a sample of this was prepared for purposes of comparison with the unknown amine. This was done by the action of ammonium formate (in the manner outlined above for the preparation of pinacolyl amine) on methyl isopropyl ketone, synthesized through hydrolysis of the bromide of tert.-amyl alcohol (180). The ketone boiled at 95°at 760 mms. and the semicarbozone melted at 112°; the amine from methyl isopropyl ketone boiled at

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(179a) Beilstein, 4th edition <u>4</u> 154.
(179b) Trasciatti, D., Gazz. chim. ital. <u>29</u> 95 (1899).
(180) Organic Synthesis, John Wiley & Sons, <u>13</u> 68 (1933).

86° at 760 mms., n_D^{25} = 1.4021. No picrate of the amine could be obtained, but the derivative with phenylisocyanate, recrystallized from benzene, melted at 130°. The melting point of a mixture of the two substituted phenyl ureas showed a depression, and this together with the difference in refractive index, and the ability of the unknown amine to form a picrate was taken as evidence of its non-identity with methylisopropylcarbinyl amine. As in the preparation of pinacolyl amine with ammonium formate, here too there appeared a small amount of a lower boiling forerun (82-86°) in the fractionation of methylisopropylcarbinyl amine, which may or may not be a different amine.

METHYLATION

In the first attempts at methylation with methyl iodide and sodium hydroxides, quantities of reagents used were in slight excess of those required when the calculations were based on the assumption that the methylation would proceed directly to the quaternary iodide. Analysis for iodine revealed, however, that the product isolated from this reaction was not the quaternary ammonium iodide $C_9H_{22}NI$, but rather the hydriodide of the tertiary amine, - N,N-dimethyl pinacolyl amine. A further proof of the identity of this product was the fact that it dissolved in aqueous sodium hydroxide, with the liberation of an amine. This amine, when collected, dried and distilled, yielded an addition product with methyl iodide, which on analysis for iodine was found to be the quaternary salt. This salt did not liberate an amine, upon dissolving it in sodium hydroxide.

N,N-DIMETHYL PINACOLYL AMINE HYDRIODIDE

A 500 cc. three necked flask, containing 27 gms. of sodium hydroxide in 250 ccs. of aqueous ethyl alcohol was fitted with a mercury sealed stirrer, a reflux condenser and a dropping funnel. After heating and stirring the mixture until the sodium hydroxide was all dissolved, the steam was shut off, and 78 ccs. of pinacolyl amine were added. Then 93 ccs. of methyl iodide were allowed to run in slowly from the dropping funnel. Care must be taken that the methyl iodide is not added too quickly, as a vigorous reaction ensues. The mixture was allowed to reflux, with stirring, for several hours after the addition of the methyl iodide, The white, crystalline material separating out on cooling was filtered off, and recrystallized from ethyl alcohol; melting point, 260-261; yield, 58%.

Anal.	wt. of substance in gms.	wt. of AgI in gms.	% iodine
	0.2590	0.2370	49.4
	0.2704	0.2482	49.6

calculated for $C_8H_{20}NI$; I =49.4%

N,N-DIMETHYL PINACOLYL AMINE

The hydriodide was dissolved in an excess of aqueous, 40% sodium hydroxide solution, and the amine was separated, dried over pellets of sodium hydroxide. On distillation, the amine was found to boil at 129-130°(759 mm.); n_D^{25} 1.4160, $D_4^{25°}$ = 0.7627. Picrate, m.p. 214°. Anal.for nitrogen (181), 0.0192 g. susbt.; 2.73 ccs. N, 754 mm., 25°C. Calc. for $C_{14}H_{22}O_7N_4$: N, 15.6%. Found: N, 15.7%.

A further quantity of tertiary amine was obtained by working up the mother liquors from the methylation. A considerable excess of aqueous-alcoholic solution of sodium hydroxide was added, and the mixture distilled into a solution of 25 ccs. of concentrated hydrochloric acid in 25 ccs. of water. Excess alcohol and water was removed from the acid solution by distillation in vacuum, the acid neutralized with excess of sodium hydroxide and the amine collected and dried. It was then distilled through a short packed column, and that fraction boiling between 125° and 128° retained. In subsequent runs, it was found desirable to proceed directly to the tertiary amine, without intermediate isolation of its hydriodide . This was done by heating and stirring a mixture of pinacolyl amine, a large excess of aqueous sodium hydroxide solution and methyl iodide. On cooling the tertiary amine formed a layer on top of the aqueous NaOH from which it was separated and distilled; yield about 80%.

(181) Allen, C.F.H. and Young, D.M. Can. J. Res. B.14 216-221 (1936).

QUATERNARY AMMONIUM IODIDE

The tertiary amine (75 gms) was mixed with an excess (45 ccs., 102.5 gms.) of methyl iodide, and 30 ccs. of benzene added to the solution. On standing for two days, white crystals of the quaternary iodide separated from the solution. These were filtered off and when recrystallized from ethyl alcohol, melted at 260°, yield 47.5%. The mixture of tertiary amine, methyl iodide and benzene, from which this first crop of crystals was filtered, upon standing for several weeks, slowly deposited more of the quaternary iodide until finally, overall yields approaching 100% were attained.

Analysis: wt. of substance in gms.	wt. of AgcI in gns.	% iodine
.2592	.2238	46.68
.2530	.2186	46.71

calculated for $C_9H_{22}NI$: I, 46.8%

PREPARATION OF OLEFINS

Before proceeding with the decomposition of the quaternary ammonium hydroxide, it seemed advisable to prepare samples of the expected olefins for purposes of comparison, and to test the efficiency of a 2.5 foot fractionating column, packed with single turn glass helicies, and of approximately 10 theoretical plates, in separating a mixture of the hydrocarbons.

Whitmore and Meunier (182) have reported that the

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(182) Whitmore, F.C. and Meunier, P.L. J. Amer. Chem. Soc. 55 3721-2 (1933).

dehydration of pinacolyl alcohol at high temperatures in the presence of phosphoric acid on silica gel as a catalyst, leads to the formation of tert.-butylethylene, unsym. methyl isopropylethylene, and tetramethylethylene in 3%, 31% and 61% yields respectively. Since these are the three possible isomers that might be expected from the decomposition of pinacolyltrimethylammonium hydroxide, pinacolyl alcohol was a convenient source for these hydrocarbons.

Tert.-butyl magnesium chloride was prepared from magnesium and tert.-butyl chloride according to Whitmore's (183) directions. Acetaldehyde was added, and the addition product decomposed and worked up in the usual manner. From a 2 mole run of tert.-butyl magnesium chloride, 94 gms. of pinacolyl alcohol, B.P. (762 mms.) 120-120.5, n_D^{20} 1.4150, were obtained. Yield, 47.7%, based on the tert.-butyl chloride.

The dehydration of the alcohol was accomplished by means of anhydrous oxalic acid (184), the anhydrous oxalic being prepared by heating the dihydrate to constant weight on the steam bath in an evaporating dish.

Seventy-five grams of pinacolyl alcohol were heated in a flask under a fractionating column with 80 gms. of anhydrous oxalic acid for several days in an oil bath at 100°-110°. At the end of three days only a few ccs. of tarry material remained in the flask. The hydrocarbons distilled

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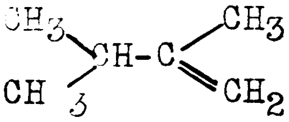
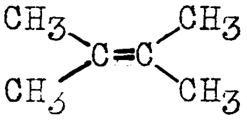
(183) Whitmore, F.C and Badertscher, D.E. J. Amer. Chem. Soc. 55 1559-1567 (1561) (1933).

(184) Whitmore, F.C. and Rothrock, H.S. J. Amer. Chem. Soc. 55 1106-1109 (1933).

between 51° and 63°; this fraction was separated and dried, weight, 45 gms., yield of hydrocarbons, 72.8%. The fraction boiling between 90°-97° was found to be chiefly water, with a little unchanged pinacolyl alcohol. The mixed hydrocarbons, after drying over potassium carbonate were carefully fractionated. In agreement with Whitmore's (183) work, when dehydrating pinacolyl alcohol with anhydrous oxalic acid, no tert.-butyl ethylene was obtained.

	unsym. methylisopropylethylene	tetramethylethylene
		
B.P. at 764 mms.	54°-57°, chiefly 56°	69°-74°, chiefly 74°
Refractive index (n_D^{20})	1.3900	1.4110
Weight in gms.	12	21
Yield %	36.4	63.6

The forerun in the fractionation of this mixture i.e. material distilling between 45°-53° - amounted to only 1 cc., and the fraction between 57° and 69° was 1.6 ccs.

PINACOLYLTRIMETHYLAMMONIUM HYDROXIDE.

Silver oxide was prepared by dissolving 113 gms. of silver nitrate in 75 ccs. of water and adding slowly 70 ccs. of 30% NaOH solution, diluted to 200 ccs. The precipitate was allowed to stand overnight; it was then filtered off, washed thoroughly with hot water, and dried at 105°.

Eighty-four grams of the quaternary ammonium iodide were dissolved on 200 ccs. of distilled water in a flask, 75 grams of silver oxide added, and the mixture stirred for several hours. After standing overnight, the precipitate of silver iodide was filtered off, and washed with distilled water to free it from the quaternary hydroxide.

DECOMPOSITION OF PINACOLYLTRIMETHYLAMMONIUM HYDROXIDE AT HIGH TEMPERATURE.

The solution of the quaternary ammonium hydroxide was placed in a 500 cc., 3 necked flask, carrying a thermometer extending below the surface of the liquid, a delivery tube for purified nitrogen, and a still head, with a thermometer. The side arm of the still head was extended below the surface of 50 ccs. of 6 N.HCl in a 500 cc. modified Claisen flask. This flask was surrounded with an ice-salt mixture. The side arm of the Claisen flask was connected to a dry ice trap, and this in turn with a trap containing a dilute solution of bromine in carbon tetrachloride. The amines, and methyl alcohol evolved in the decomposition were collected in the acid solution, while the olefins were caught in the dry ice trap. The bromine solution was not decolourized during the run, showing that there was no loss of olefin.

A very gentle stream of purified nitrogen was passed through the system, and the flask containing the hydroxide solution was heated in an oil bath to distill off the water. During this period, the thermometer in the still head indicated a temperature of 100°. As more water was removed, however, the hydroxide began to decompose and the temperature of the vapours fell to as low as 70°. Meanwhile the temperature of the liquid in the flask slowly rose from 100° to 160° - at which point almost no residue was left in the flask, and the heating was stopped.

Water was removed from the acid solution in the Claisen flask by distillation under reduced pressure. The first 10 ccs. of distillatewere separated and tested for methyl alcohol. A derivative of this liquid obtained with 3,5 dinitrobenzoyl chloride, melted at 107°.
The melting point of the 3,5 dinitrobenzoate of methyl alcohol is 107° (185). No attempt was made to estimate the methyl alcohol quantitatively. Removal of the water was continued until a white solid crystallized out in the flask. This solid, consisting of trimethylaminehydrochloride, N.N-dimethyl-pinacolyl aminehydrochloride or a mixture of both, was redissolved in 100 ccs. of water and transferred to a 500 cc. three necked flask under a fractionating column. One hundred ccs. of 50% NaOH solution were added, and then purified nitrogen was passed below the surface of the solution. The nitrogen served to sweep out the gaseous trimethylamine, which was condensed in a dry ice trap at the top of the column. The

(185) Kamm, O., Qualitative Organic Analysis, John Wiley and Sons 1932, p.166.

flask containing the amine solution was warmed to 90° for 2 hours during the passage of the nitrogen. At the end of this time, 7 grams of condensate were obtained in the dry ice trap; this was dissolved in water, a small, insoluble layer on top assumed to be N,N-dimethyl pinacolyl amine being returned to the original flask, and a picrate made of the amine in the aqueous solution, m.p. 216° . The picrate of a known sample of trimethyl amine melted at 216° , and a melting point of the mixture of these two showed no depression.

The amine remaining in the flask was separated from the sodium hydroxide solution, dried over pellets of NaOH and weighed 17 grams. The picrate made from this amine melted at 214° , and the melting point of a mixture of this with an authentic sample of the picrate of N,N-dimethyl pinacolyl amine was 214° .

The hydrocarbons resulting from the decomposition of the quaternary hydroxide were collected in the dry ice trap. This liquid was dried over anhydrous potassium carbonate, and weighed 8 grams. Then it was carefully fractionated through the packed column, at a reflux ratio of 1:10. Although the liquid distilled at 40.3°- 40.6° at 760 mms., the distillate was divided into three fractions. The refractive index of each was taken in an endeavour to find traces of an olefin other than tert.-butylethylene. These data are recorded in the table on page 100 , and from the constancy of the boiling point and the refractive indices it was concluded that no other olefin was present, in any measurable amount.

DECOMPOSITION OF PINACOLYLTRIMETHYLAMMONIUM HYDROXIDE AT ROOM TEMEPRATURE.

An aqueous solution of pinacolyltrimethyl ammonium hydroxide was prepared by stirring together for several hours, allowing to stand overnight, and then filtering through asbestos, a mixture of 75.5 grams of pinacolyltrimethyl ammonium iodide, 65 grams silver oxide, and 100 ccs. distilled water.

The clear, but dark coloured solution was placed in a Claisen flask (tare 200.0 grams) and the water removed by distillation under a pressure of 15-20 mms., a fine capillary, drawing air through a sodium hydroxide drying tower serving to promote even boiling. A water bath around the Claisen flask was maintained at 25° - 30° . The distillation was continued in this manner until a white solid began to precipitate out in the flask, and the contents became rather slushy in consistency. The flask was then connected by pressure tubing to a system consisting first, of a trap in a solid CO_2- acetone bath (delivery tube 15 cms. below the level of the liquid in the bath), then to a trap immersed in liquid air (delivery tube 23 cms. below the level of the liquid air) and finally to two mercury vapour pumps backed by an oil pump. By this means, a pressure of 0.01-0.005 mms.

as registered on a McLeod gauge was maintained in the apparatus. The pumps were operated only during the day, but the pressure was kept fairly low (3 mms) at night by closing a stop cock between the liquid air trap and the first mercury pump prior to shutting off the pumps.

After two days of such treatment, the contents of the flask had completely crystallized, and looked quite dry. At about the same time, a smell of amine became apparent in the traps, which indicated the beginning of the decomposition. Accordingly, all the previous condensate (water) was removed from the traps, and the weight of flask and contents was found to be 253.5 grams, the contents therefore weighing 53.5 grams. The subsequent rate of decomposition was followed by opening the system and weighing the flask from time to time. In spite of the fact that the inlet tubes of the traps were made of large-bore tubing, (7mms.) it was found necessary to remove the rubber stoppers from the mouths of the traps about every three days and to allow the plug of solidified condensate to melt sufficiently to permit its sliding down into the trap. During the first two weeks, the decomposition proceeded at approximately at the rate of two grams of quaternary hydroxide decomposing per day; but as the reaction continued, the rate became slower and slower, until finally, after a total of three and a half weeks, (with 7.5 grams of hydroxide still to decompose) the flask was loosing in weight less than half a gram per day. The reaction was stopped at this stage, when the flask had decreased in weight by a total of 46.0 grams an amount corresponding to 86.5% complete decomposition,

The condensate in the two traps was combined and weighed- 43.5 grams- showing the loss of only 2.5 grams of material evolved in the decomposition and not condensed in the traps.

To the condensate was added 150 ccs. of distilled water and the upper, hydrocarbon layer was separated, washed with three portions of 3% HCl (to remove amine), once with distilled water, twice with 2% potassium carbonate solution, then with distilled water, and finally dried over powdered sodium hydroxide. The hydrocarbon (13.0 grams, 64.8% yield, based on the amount expected from 86,5% decomposition of the hydroxide) was distilled through the packed column, already described, and divided into fractions, The hold-up from this column, amounting to about 2 ccs. was transferred to a two cc. flask with side arm, and distilled until only 0.1 cc. residue was left. The physical constants of the various fractions obtained are shown in the table on page 101.

The aqueous solution of amine was first acidified with dilute HCl and warmed, to allow the separation of any dissolved hydrocarbon; however none was observed, Accordingly the solution was made alkaline again and placed in a flask under the packed column. A gentle stream of pure dry nitrogen was bubbled through, and the mixture warmed; the distillate was condensed in a dry ice-acetone trap at the top of the column. This condensate was then completely distilled at room temperature into a receiver containing distilled water, in which it all dissolved.

Inasmuch as there was no residue after distillation at room temperature, and since the amine dissolved completely in water, it was concluded that no N,N-dimethylpinacolylamine had been formed.

DECOMPOSITION OF THE MONOXANTHATE OF 2,3-BUTYLENE GLYCOL.

In a three-necked flask, fitted with a stirrer and a reflux condensed were placed 50 grams of 2.3-butylene glycol (from Eastman Kodak Company, redistilled b.p. 86° at 10 mms) and 150 ccs. of toluene. The stirrer was started, and 12.8 grams (equivalent to one hydroxyl group) of sodium cut in small pieceswere added, and the mixture refluxed until all the sodium had disappeared. After cooling, 40 ccs. of carbon disulphide were added and the mixture again allowed to reflux for several hours. Then 40 ccs. of methyl iodide were added and the mixture allowed to stand over night.

The next day, the solution was filtered, the clear supernatant yellow liquid being decanted from the white, inorganic precipitate. This salt was found to be exceedingly sticky, and difficult to dry by suction. However the small amount of liquid which was finally separated from the solid was found to be insoluble in the main portion of the filtrate, to be much deeper in colour (reddish brown) and of greater density than the toluene solution.

The toluene solution was separated from the small amount of dark coloured, oily liquid, and the toluene was removed by distillation through the packed column, described earlier. Unless a column were used, the distilled toluene was found to have a distinct yellow colour. The liquid remaining in the distilling flask was dissolved in 75 ccs. of ether, and washed with water to remove inorganic salts, and any unchanged glycol. The mixture was dried over potassium carbonate, and the ether removed by distillation. Remaining behind were 73 grams of the mono-xanthate ester of the glycol (73% yield). The xanthate was transferred to a flask fitted with a reflux air condenser, the top of which was connected to a tube leading to a receiver in a solid CO_2-acetone bath. Then the xanthate was refluxed daily for one week at such a rate that the vapours rose part way in the condenser, but no visible distillation took place. The bath was heated to about 200^o. At the end of a week when the volume of liquid in the receiver was 25 ccs.- approximately that expected from the decomposition of 73 grams of xanthate to give methyl mercaptan, and when the rate of refluxing became very slow, even at somewhat higher temperature, the decomposition was judged to be over, and the heating stopped.

To detect the presence of any carbon oxysulphide in the liquid in the receiver, the liquid was redistilled. Since carbon oxysulphide boils at -50°C. and methyl mercaptan at 7.6° if any of the former were present, it would be expected to distill from the mixture when the flask was placed in an ice-water bath at 0°C. With the addition of several chips of porous plate, this was done, but no distillation observed. The temperature was then gradually raised until the methyl mercaptan began to distil and it was again collected in the solid carbon dioxide-acetone trap. After the temperature of the flask had risen to 25°C., and the distillation of methyl mercaptan was complete, there remained in the flask 5 ccs. of a higher boiling liquid, from which there precipitated on standing an unidentified white solid. The liquid was filtered, and identified as methyl ethyl ketone through its boiling point, (78° at 760 mms.) and by the fact that no depression was observed in the melting point of a mixture of its 2.4-dimitrophenylhydrozone (m.p. 110°) with the same derivative of a known sample of methyl ethyl ketone, also melting point at 110°.

The product remaining from the pyrolysis of the xanthate, and thought to be the cyclic thiocarbonate, was distilled in vacuum from a small amount of tar, and was found to be an reddish-orange liquid, with not too disagreeable an odour.

This liquid, amounting to about 25 ccs. was distilled a second time in vacuum, apparently without decomposition, and divided into approximately three equal fractions. The second of these portions was in turn, fractionated in vacuum, and divided, as before into three parts. The results are contained in the following table:

Fractionation of the distilled liquid:

Fraction	1	2	3
Temperature in degrees C.	85-90	90	90-92.5
Pressure in mms. of Hg.	10	10	10
Approx. Vol. in ccs.	5	10	10

Fractionation of fraction 2 above:

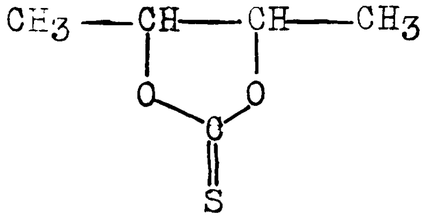
Fraction	1A	2A	3A
Temp. in ^{o}C	86	87	86.8-88
Press.in mms.Hg.	9	8	8
Vol. in ccs.	2	6	1
d_4^{25}		1.216	
n_D^{25}		1.6082	

The liquid of fraction 2A was analysed for sulphur by the Carius bomb method, but results were consistently low, possibly due to traces of toluene still in the liquid.

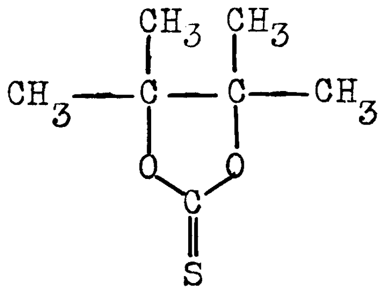
Analysis: wt. of subs. in gms.	wt. of $BaSO_4$	% S
0.0936	0.1498	22.0
0.0687	0.1128	22.4
0.1006	0.1644	22.6
	average	22.5

Calculated for $C_5H_8O_2S$; % S = 24.2

The calculated molecular refraction (using the value 9.48 for the atomic factor for thioketo sulphur, derived from the molecular refraction of carbon disulphide) is 31.23, while the observed value is 37.57. This increase, which is greater than the exaltation normally to be expected from the presence of a heterocyclic ring, can only be explained as due to the probable impurity of the compound in question. There can be little doubt as to the correctness of the assigned structure i.e.



of this compound, especially since Fomin (185a) had obtained the analogous compound



from the monoxanthate of pinacol. This material was a solid, melting at 145°, and was hydrolysed to pinacol hydrate, potassium carbonate, and potassium sulphide by strong potassium hydroxide. Hydrolysis with strong acids resulted in the formation of pinaclone.

In order to hydrolyse the cyclic thiocarbonate and

(185a) Fomin V.A., J. Gen. Chem. (U.S.S.R.) <u>5</u> 1192-4 (1935).

recover the original glycol, 2.5 grams of fraction 3 were refluxed over night on the steam bath with an aqueous alcoholic solution of sodium hydroxide. The next day, the white solid which had precipitated was filtered off, and found to evolve H_2S with mineral acids. The alcohol and water were removed from the filtrate by distillation- the temperature rising to, but at no time exceeding 101°C. Nevertheless, there was a small amount (0.5 cc.) of high boiling liquid which was transferred to a micro fractionation apparatus and divided by distillation into three fractions. The boiling point of the third one was determined by Siwoloboff's micro method (186) and found to be 180°C. (760 mms.) A known sample of 2,3-butylene glycol boiled at the same temperature in the same apparatus.

A qualitative test for 2,3 butylene glycol on (187) the distillate boiling up to 101° gave a positive result. This was done by adding to 5 ccs. of the solution thought to contain the glycol, several drops of a saturated solution of bromine in water. After heating on the steam bath for a few minutes, the glycol was oxidized to 1-hydroxyethylmethyl ketone, $CH_3CO-CH(OH)CH_3$, and excess bromine was removed by adding dropwise the required amount of 20% sodium sulphite solution. Then 5 ccs. of 45% ferric chloride was added to carry the oxidation to diacetyl, the mixture refluxed for several minutes, and then 3-4 ccs. of

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(186) Morton, A.A. Laboratory Technique in Organic Chemistry, McGraw-Hill Book Co., New York, 1938 P. 51.

(187) Moureu, H., and Dode, M. Bull. assoc. Chem. sucr. dist. 51 247-50 (1934); Chem. Abs. 28 6239(1934). Lemoigne, M., Compt. rend. 170 (131-2 (1920).

distillate collected. Fifteen to twenty drops of aqueous ammonium hydroxide were added to the distillate, followed by five drops of 20% aqueous hydroxylamine hydrochloride, five drops of 10% aqueous nickel chloride and the mixture boiled. On cooling, a red characteristic microcrystalline precipitate of nickel dimethylglyoxime appeared, indicating the presence in the original solution, of 2,3 butylene glycol.

Decomposition of the xanthate of benzhydrol.

Forty grams of benzhydrol were dissolved in 75 ccs. of toluene, contained in a 500 cc. three necked flask, fitted with mechanical stirrer and a reflux condenser. Five grams of sodium were added, and the mixture refluxed and stirred for eight hours. After cooling, the small amount of excess sodium was removed, and 20 ccs. of carbon disulphide added, followed by 25 ccs. of methyl iodide. The following day, the white inorganic solid was filtered off and the yellow toluene solution washed with water to remove sodium iodide, and dried over anhydrous sodium sulphate. The toluene was removed by vacuum distillation, leaving 48 grams of methyl xanthate ester. (80.5% yield). The ester was then heated for 12 hours in a small Claisen flask in a sand bath, the temperature of the latter being 330°. The distillate was collected in a dry ice trap and any non-condensable gas was passed through aqueous barium hydroxide solution. The material in the dry ice trap was found to consist, in addition to a small amount of methyl mercaptan, mainly of carbon disulphide and traces of a higher boiling liquid, possibly methyl disulphide. The slow formation of a white precipitate in the barium hydroxide solution, indicated the presence of carbonoxysulphide.

The residue in the Claisen flask was distilled in vacuum, and 19.5 grams of a yellow oil, boiling point 135 - 140° at 15 mms. collected; a further two grams of this same material was obtained by steam distilling in the presence of sodium hydroxide, the residue from the vacuum distillation. The oil was collected by extraction with ether, dried over anhydrous potassium carbonate, the ether removed, and the remaining oily solid recrystallized from ethyl alcohol - water; it was identified as diphenylmethane through comparison of its odour with a known sample, and from its melting point (24-25°), total yield, based on benzhydrol used, 58.8%.

The residue from the vacuum distillation was boiled with alkali to bring about the formation of a sodium salt of either the hydroxy, or the thio hydroxy acid formed by elimination of a γ hydrogen during the decomposition. After refluxing for several hours, the insoluble material was filtered off, and the alkaline solution made acidic - whereupon a very small amount of a brown, rather tarry substance was precipitated. On filtration, not more than 0.1 gm. of solid was obtained; this was soluble in sodium carbonate solution, and could be reprecipitated upon the addition of acid. Lack of material prevented further purification and hence, attempts to elucidate the structure. However, from its ready solubility in cold aqueous sodium carbonate it is rather unlikely to be the lactone expected from γ elimination of hydrogen and subsequent ring formation.

The residue from the decomposition mentioned above as being insoluble in alkaline solution, and which had been removed by filtration, (weight 11 gms. yield 30%) was clarified by treatment with animal charcoal in benzene solution, and recrystallized from benzene. The melting point was found to remain constant at 208-209° - a value not corresponding with Kursanoff's (188) 223-4° for tetraphenylethylene, but agreeing with the one reported (189) for tetraphenylethane. Accordingly a sample of the latter material was synthesized from diphenylmethane, via the bromide, and a coupling reaction by zinc in ethyl acetate, after the manner described by Norris, Thomas and Brown (190). The tetraphenylethane so obtained, melted at 209° (recrystallized from benzene). Since the melting point of the mixture of these two substances showed no depression, it was concluded that the decomposition of the methyl xanthate ester of benzhydrol yielded tetraphenylethane, together

(188) Kursanoff, D.N., J. Russ. Chem. Soc., Chem. Part <u>60</u> No.6 921-4 (1928).
(189) Beilstein, 4th Ed. <u>5</u> 740.
(190) Norris, J.F., Thomas, R., Brown, B.M., Ber. <u>43</u> 2940-59 (1910).

with diphenylmethane and the various sulphur compounds mentioned above, and not tetraphenylethylene as previously reported by Kursanoff.

SUMMARY

1. Pinacolyltrimethylammonium hydroxide - a compound possessing a carbon skeleton particularly prone to undergoing rearrangement during chemical reactions - has been decomposed at high temperatures, and at room temperature. In both cases, only the unrearranged olefin, tert.-butylethylene was isolated; at 160°, the decomposition proceeded to the extent of 48% to yield trimethylamine and the hydrocarbon, and 52% to give methyl alcohol and the mixed tertiary amine. At room temperature, the olefin and trimethylamine were the sole products obtained.

2. The monoxanthate ester of 2,3 butylene glycol has been decomposed and methyl ethyl ketone and a cyclic thio carbonate have been isolated; these are products resulting from the elimination of a beta and a gamma hydrogen atom respectively.

3. The decomposition of methylbenzhydrylxanthate has been studied; the products obtained were diphenylmethane and tetraphenylethane and not tetraphenylethylene as reported by Kursanoff. Only a trace of material was isolated corresponding to the expected thiolactone which might be formed by gamma bonding, elimination and ring closure. The formation of the saturated hydrocarbons suggests free radical formation rather than alpha or gamma elimination.

4. In the light of these results, Ingold's theory of the mechanism of decomposition of quaternary ammonium bases has been modified to include hydrogen bond complex formation. These same views have been extended to include the decomposition of xanthate esters - a reaction for which no mechanism has hitherto been proposed.

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