not much of a difference in the ease of hydrolysis of the three chlorines under the conditions used.

Infrared spectra. Spectra were obtained on a KM-1 Baird-Atomic infrared spectrophotometer. Matched 1 mm. sodium chloride cells were used for the solution spectra. Pure liquids were run as thin films between two sodium chloride plates. All bands reported were calibrated against the nearest polystyrene peaks run on each chart. Because all of the compounds were found to be sufficiently soluble in benzene, it was the common solvent used to compare the spectra of the various compounds. The compounds were also run in other solvents in order to examine the regions of the spectra that were masked by strong benzene absorbing bands. Thus, the spectrum of compound I was also obtained in carbon tetrachloride, compound II in carbon tetrachloride, and phosphorus trichloride, and compound IV in phosphorus trichloride. There are a few extra bands that appear in these latter spectra that do not appear in the benzene spectra.

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WACO, TEX.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Pyrolysis of γ-Hydroxyalkyl Quaternary Ammonium Hydroxides and Alkoxides. Acyclic Systems[1,2]

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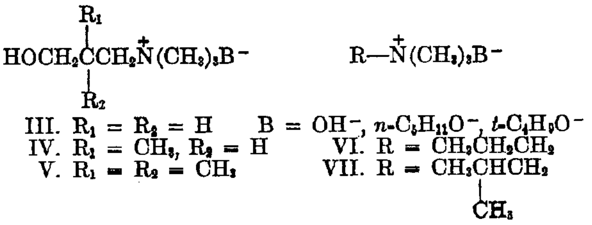
The decomposition of hydroxyneopentyltrimethylammonium hydroxide proceeds by dequaternization to produce 2,2-dimethyl-3-dimethylaminopropanol-1 (34%) plus the corresponding methyl ether (15%) and by a 1,3-cleavage (40%) to isobutylene, trimethylamine, and formaldehyde (although this undergoes further reaction in base). As the anion in this pyrolysis was changed to *n*-pentyl oxide and *t*-butoxide, the 1,3-cleavage increased up to 80%. When 3-hydroxypropyl- or 3-hydroxyisobutyltrimethylammonium hydroxide or *t*-butoxide was decomposed, Hofmann elimination was the predominant reaction leading to allyl alcohol and methallyl alcohol, respectively. The yield of elimination in these compounds appeared to be independent of the base used which was not the case for isobutyltrimethylammonium hydroxide (63%) and *t*-butoxide (20%). Apparently the hydroxyl group in the 3-position facilitates the Hofmann elimination. When Hofmann elimination is possible in these acyclic systems, this reaction predominates over the 1,3-cleavage.

When a hydroxylalkyl group is present in a quaternary ammonium base, the following equilibrium may arise:

$$\underset{\text{I}}{HO{-}(CH_2)_n{-}\overset{+}{N}(CH_3)_3B^-} \rightleftarrows \underset{\text{II}}{{}^-O{-}(CH_2)_n{-}\overset{+}{N}(CH_3)_3} + BH$$

One effect of the hydroxyl or alkoxide group in the decomposition reaction has been the formation of 3-,[4-7] 5-,[8] and 7-[9]membered oxygen heterocycles; while in the 2-hydroxyalkyl ($n=2$) group it also enhances elimination by an inductive effect.[10] In the case of 3-hydroxyalkyl quaternary ammonium hydroxides[11-13] only olefin formation was observed in unreported yields. This paper deals with the decomposition of the following 3-hydroxyalkyl quaternary ammonium hydroxides and alkoxides.



$HOCH_2\overset{R_1}{\underset{R_2}{C}}CH_2\overset{+}{N}(CH_3)_3B^-$ $\qquad R{-}\overset{+}{N}(CH_3)_3B^-$

III. $R_1 = R_2 = H$ $\quad B = OH^-, n\text{-}C_5H_{11}O^-, t\text{-}C_4H_9O^-$
IV. $R_1 = CH_3, R_2 = H$ $\quad$ VI. $R = CH_2CH_2CH_3$
V. $R_1 = R_2 = CH_3$ $\quad$ VII. $R = CH_2\underset{CH_3}{CH}CH_3$

The various types of reactions one could consider for the decomposition of 3-hydroxyalkyltrimethylammonium bases are summarized in the equations below.

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[1] This work was supported by a Frederick Gardner Cottrell Grant from Research Corp. for which grateful acknowledgement is made.

[2] Presented at the 134th Meeting of the American Chemical Society at Chicago, Ill., in September, 1958.

[3] Abstracted from the Ph.D. Dissertation of J. G. D., May 1960.

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[5] H. W. Bersch and G. Hubner, *Arch. Pharm.*, **289**, 673 (1956).

[6] B. Witkop and C. M. Foltz, *J. Am. Chem. Soc.*, **79**, 197 (1957).

[7] M. Svoboda and J. Sicher, *Collection Czechoslov. Chem. Commun.*, **23**, 1540 (1958).

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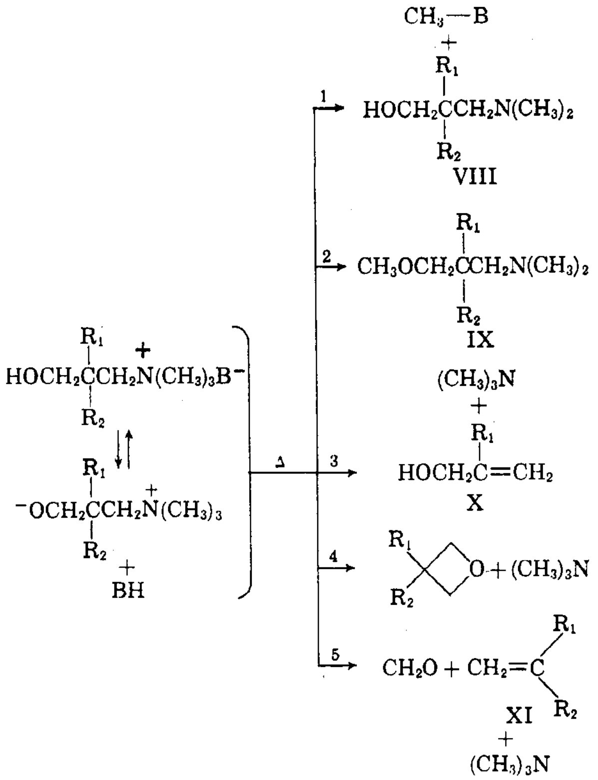
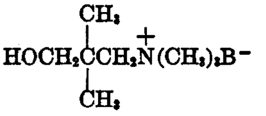
[13] C. Schopf, G. Dummer, W. Wust, and R. Rausch, *Ann.*, **626**, 134 (1959).

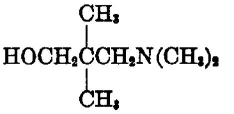
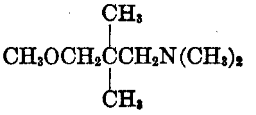
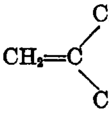


When compound V ($B = OH^-$) was heated to 125°, decomposition proceeded smoothly and the following products were isolated: 2,2,-dimethyl-3-dimethylaminopropanol-1 (VIII, $R_1 = R_2 = CH_3$), 34%; 2,2-dimethyl-3-dimethylamino-1-methoxypropane (IX, $R_1 = R_2 = CH_3$), 15%; isobutylene (XI, $R_1 = R_2 = CH_3$), 40%; and trimethylamine, 22–46%. The identity of VIII, $R_1 = R_2 = CH_3$ was established by physical constants, comparison of the infrared spectrum with an authentic sample, and preparation of a methiodide. The structure of IX, $R_1 = R_2 = CH_3$ was proved by comparison of physical constants, methiodide, and infrared spectrum with those of an authentic sample prepared by a Williamson synthesis with methyl chloride and the sodium salt of VIII, $R_1 = R_2 = CH_3$. Isobutylene was characterized by conversion to 1,2-dibromo-2-methylpropane and 1,2,3-tribromo-2-methylpropane, while a picrate and hydrochloride of trimethylamine were prepared.

Reaction 1 represents the usual consequences when olefin formation is impossible as in neopentyltrimethylammonium hydroxide,[14] while paths 2 and 5 describe the role of the 3-hydroxy group. Of the compounds in Equation 5, the amounts of isobutylene and trimethylamine were comparable but only a trace of formaldehyde was obtained as the 2,4-dinitrophenylhydrazone; however, the bulk of this product probably underwent the Cannizzaro reaction in the presence of strong base. Analogous 1,3-cleavage reactions (path 5) have been described in the literature[15–20] and recently Grob[21] has summarized these reactions by his "principle of ethylogy." In this particular example the quaternary ammonium hydroxide is in equilibrium with the dipolar ion which has attached to one end of a three carbon chain an electron rich atom (O^-) and at the other end an electron seeking atom ($-\overset{+}{N}(CH_3)_3$). Evidence for this intermediate was found when the decomposition of V, $B = n-C_5H_{11}O^-$ in n-pentyl alcohol and V, $B = t\text{-}C_4H_9O^-$ in t-butyl alcohol was carried out in refluxing alcohol for forty-eight hours. A summary of these data is found in Table I. When compound VIII, $R_1 = R_2 = CH_3$ was refluxed with potassium t-butoxide in t-butyl alcohol for four hours, no olefin or base was evolved and the starting amino alcohol was recovered in 87% yield. Thus all the isobutylene and base evolved in the decomposition of V, $B = n\text{-}C_5H_{11}O^-$ and V, $B = t\text{-}C_4H_9O^-$ must result from a 1,3-cleavage reaction of the quaternary base. The enhancement of this reaction is in the direction of increased concentration of dipolar ion which results from increased base strength.

TABLE I

Pyrolysis of 
$HOCH_2C(CH_3)_2CH_2\overset{+}{N}(CH_3)_3B^-$

Product	Yield, %		
	$B = OH^-$	n-$C_5H_{11}O^-$	t-$C_4H_9O^{-a}$
 $HOCH_2C(CH_3)_2CH_2N(CH_3)_2$	34	11	6
 $CH_3OCH_2C(CH_3)_2CH_2N(CH_3)_2$	15	1	2
 $CH_2{=}C(CH_3)_2$	40	58 (71)[b]	75
$(CH_3)_3N$	23–46	70	81

[a] Yields are based on unrecovered methiodide. [b] Based on the conversion to a mixture of crude dibromide and tribromide.

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(15) H. R. Snyder and J. H. Brewster, *J. Am. Chem. Soc.*, **71**, 1061 (1949).

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(18) R. B. Clayton, H. B. Henbest, and M. Smith, *J. Chem. Soc.*, 1982 (1957).

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(21) C. A. Grob, *Experientia*, **13**, 126 (1957).

Ether formation *via* path 2 may arise by methylation of the oxide anion of VIII, $R_1 = R_2 = CH_3$ or it may involve the dipolar ion as an intermediate. Since the yield of ether IX, $R_1 = R_2 = CH_3$ was decreased markedly when stronger bases were used, this reduces the attractiveness of the dipolar ion as an intermediate in the formation of this compound.

The pyrolysis of compounds III, $B = OH^-$ and IV, $B = OH^-$ gave products explained by reaction paths 1 and 3. From III, $B = OH^-$ was obtained allyl alcohol 79% (determined by titration[22]), identified by physical constants and a 3,5-dinitrobenzoate derivative; trimethylamine 81%, characterized by its picrate and VIII, $R_1 = R_2 = H$ 6% identified by conversion to the methiodide. Pyrolysis of IV, $B = OH^-$ gave methallyl alcohol (X, $R_1 = CH_3$) 67% physical constants and the α-naphthylurethan derivative established the structure; trimethylamine 71% identified by its picrate and VIII, $R_1 = CH_3$, $R_2 = H$ 16% characterized by physical constants and methiodide.

Since more 1,3-cleavage occurred in the decomposition of V with increased base strength, similar experiments were performed with III, $B = t\text{-}C_4H_9O^-$ and IV, $B = t\text{-}C_4H_9O^-$. These data are summarized in Table II and indicate that in these cases the extent of reaction by path 1 and 3 does not depend on the nature of the base.

TABLE II

Decomposition of $HOCH_2\overset{R}{C}HCH_2\overset{+}{N}(CH_3)_3B^-$

	Yield, %			
	R = H		R = CH_3	
Product	B = OH^-	$t\text{-}C_4H_9O^-$	OH^-	$t\text{-}C_4H_9O^-$
$CH_2{=}\overset{R}{C}{-}CH_2OH$	79	75	67	50
$CH_2{=}\overset{R}{C}{-}CH_2OCH_3$	—	1	—	6
$(CH_3)_3N$	81	87	71	70
$(CH_3)_2NCH_2\overset{R}{C}HCH_2OH$	6	3	16	14

When one compares the extent of Hofmann elimination in III, $B = OH^-$ and IV, $B = OH^-$ with that from the corresponding n-propyltrimethylammonium hydroxide[10] and i-butyltrimethylammonium hydroxide[10] (Table III), the similarity in yields is not surprising since a γ-hydroxyl group would not be expected to contribute appreciably to the steric hindrance of or, by induction, increase the acidity of the β-hydrogen atom. However, the comparable yields of olefinic material from the hydroxyalkyl quaternary ammonium hydroxides and t-butoxides are less compatible with the E_2 mechanistic scheme,[23] because of the vast difference in steric bulk of these anions.

Ingold and Patel[24] have studied the decomposition of i-butyltrimethylammonium hydroxide, methoxide and ethoxide (data in Table III) and showed a slight decrease in elimination when bulkier bases, even though stronger, were used. This series was extended to include n-propyltrimethylammonium t-butoxide and i-butyltrimethylammonium t-butoxide and i-butoxide. The choice of i-butoxide was made on the assumption that this anion is sterically similar to the dipolar ion IV which may act intermolecularly as the attacking base. These results appear in Table III and clearly indicate, especially in the isobutyltrimethylammonium system, that a bulky base gives less Hofmann elimination and more dequaternization to the corresponding dimethylalkylamine.

Since the Hofmann elimination in IV, $B = OH^-$ and IV, $B = t\text{-}C_4H_9O^-$ (70% for both based on trimethylamine evolution) is similar and 3.5 times greater than elimination in VII, $B = i\text{-}C_4H_9O^-$, this suggests that a common intermediate as the dipolar ion from both IV, $B = OH^-$ and IV, $B = t\text{-}C_4H_9O^-$ may be present and that this intermediate facilitates the formation of olefin. This effect may be explained by a neighboring group participation by the alkoxide ion in removing intramolecularly the β-hydrogen, thus initiating the elimination; or, the ability of the dipolar ion to compete according to path 1, as compared to a simple alkoxide anion, is decreased to such an extent that the alternate elimination reaction (path 3) predominates. These points are under consideration.

EXPERIMENTAL[25]

Dimethyl-n-propylamine, dimethyl-i-butylamine and 3-dimethylaminopropanol-1. The Eschwieler-Clark[26] procedure was employed for the preparation of these compounds.

n-Propylamine (40 g., 0.68 mole), 90% formic acid (200 g., 3.9 moles), and 40% formalin (137 g., 1.7 moles) were converted to 40 g. (68%) of dimethyl-n-propylamine, b.p. 63–64°, n_D^{20} 1.3869 (lit.,[27] b.p. 65.5° (752 mm.), n_D^{20} 1.3866).

Employing the above mole ratios, i-butylamine (50 g., 0.68 mole) gave 41 g. (59%) of dimethyl-i-butylamine, b.p. 79–81°, n_D^{20} 1.3928 (lit.,[27] b.p. 81° (753 mm.), n_D^{20} 1.3907).

From 3-aminopropanol-1[28] (75 g., 1.0 mole), 90% formic acid (255 g., 5.0 moles) and 37% formalin (180 g., 2.2 moles)

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[22] A. Polgar and J. L. Jungnickel, *Organic Analysis*, Vol. 3, Interscience, New York, 1956, p. 240.

[23] H. C. Brown and I. Moritani, *J. Am. Chem. Soc.*, 78, 2203 (1956).

[24] C. K. Ingold and C. S. Patel, *J. Chem. Soc.*, 68 (1933).

[25] All melting points and boiling points are uncorrected. The carbon and hydrogen analyses were determined by Midwest Microlabs Inc., Indianapolis, Ind. Infrared spectra were recorded on a Baird Associates infrared spectrophotometer by R. F. Love and C. Lynch.

[26] M. L. Moore, *Org. Reactions*, 5, 323 (1949).

[27] J. Hansson, *Svensk. Kem. Tidskr.*, 67, 258 (1958).

[28] This sample was kindly donated by The American Cyanamid Co.

TABLE III

Decomposition of $CH_3\overset{R}{\overset{|}{C}}HCH_2\overset{+}{N}(CH_3)_3B^-$

		Yield, %							
		R = H		R = CH_3					
	B^- =	OH^-	t-$C_4H_9O^-$	OH^-	CH_3O^-	$C_2H_5O^-$	i-$C_4H_9O^-$	i-$C_4H_9O^-$	t-$C_4H_9O^-$
Product	Solvent		t-C_4H_9OH				t-C_4H_9OH	i-C_4H_9OH	t-C_4H_9OH
$CH_3\overset{R}{\overset{\vert}{C}}{=}CH_2$		84^b	64^a	63^b	57^c	55^c	6	17^a	29^a
$(CH_3)N_3$		N.R.	67	N.R.	N.R.	N.R.	19	21	32
$CH_3\overset{R}{\overset{\vert}{C}}HCH_2N(CH_3)_2$ titrated		N.R.	33	N.R.	N.R.	N.R.	71	73	59
$CH_3\overset{R}{\overset{\vert}{C}}HCH_2N(CH_3)_2$ isolated			13				54	52	36

N.R. = not reported. [a] Yields determined as the bromine adduct. [b] See ref. 10. [c] See ref. 24.

was isolated 66 g. (64%) of 3-dimethylaminopropanol-1, b.p. 160–164°, n_D^{20} 1.4360 (lit.,[29,30] b.p. 163–164°).

Methyl β-dimethylaminoisobutyrate. A cold solution of dimethylamine (46.4 g., 1.03 moles) in 100 ml. of methanol and cold methyl methacrylate (105 g., 1.05 moles) in 200 ml. of methanol were mixed and allowed to stand at room temperature 4 days. Distillation through a 12-in. Vigreux column gave 135 g. (92%) of methyl β-dimethylaminoisobutyrate, b.p. 152–154°, n_D^{20} 1.4187. An analytical sample had the following physical constants: b.p. 154°, n_D^{20} 1.4190.

Anal. Calcd. for $C_7H_{15}NO_2$: C, 57.90; H, 10.41. Found: C, 57.84; H, 10.38.

2-Methyl-3-dimethylaminopropanol-1. Methyl β-dimethylaminoisobutyrate (72.5 g., 0.50 mole) in 300 ml. of ether was added with stirring over a 10-hr. period to a slurry of of lithium aluminum hydride (12.0 g., 0.317 mole) in 200 ml. of ether and the mixture was refluxed for 1 hr. After the addition of water (23 ml.) and sodium hydroxide (17 g., 0.42 mole) in 25 ml. of water, the ether layer was separated and dried over sodium sulfate. Distillation gave 52 g. (89%) of 2-methyl-3-dimethylaminopropanol-1, b.p. 159–160°, n_D^{20} 1.4325.

Careful fractionation of 18.8 g. through a 0.8 × 25 cm. electrically heated column packed with $^1/_{16}$ in. glass helices and equipped with a variable take off head gave 15.2 g. (81%) of pure amine, b.p. 62° (20 mm.), n_D^{20} 1.4325.

Anal. Calcd. for $C_6H_{15}NO$: C, 61.59; H, 12.90. Found: C, 61.82; H, 13.04.

2,2-Dimethyl-3-dimethylaminopropanol-1. A solution of 70.0 g. (0.55 mole) of 2,2-dimethyl-3-dimethylaminopropanal, b.p. 146–148°, n_D^{20} 1.4245 (prepared by the procedure of Mannich, Lesser, and Silten[31]) in 600 ml. of water was added with stirring over a period of 2.5 hr. to a solution of sodium borohydride (8.2 g., 0.22 mole) in 100 ml. of water and the mixture refluxed for 2 hr. After the addition of 120 ml. of concd. hydrochloric acid, the solution was made alkaline with sodium hydroxide (88 g., 2.2 moles), saturated with sodium chloride and extracted with ether. Distillation of the dried extract gave 56 g. (78%) of 2,2-dimethyl-3-dimethylaminopropanol-1, b.p. 67–69° (15 mm.), n_D^{20} 1.4343 (lit.,[31] b.p. 166–168°).

Preparation of methiodides. These compounds were obtained according to standard procedures. Analytical samples were prepared by recrystallization to constant melting point from absolute ethanol and/or ethyl acetate. Table IV contains the experimental conditions, yields and physical constants of the methiodides.

General procedures for decompositions. Method A. Decomposition of quaternary ammonium hydroxides. Preparation of the quaternary hydroxides. An aqueous solution (10–20%) of the quaternary iodide was passed through a 125 × 3.5 cm. column of Dowex 2 × 7.5 (20–50 mesh) anion exchange resin[33] in the hydroxide form followed by a thorough washing with distilled water. Conversion to hydroxide was 90–97% with a material balance of 95% or more. Iodide ion content was measured by the Volhard method.

Apparatus. The decomposition pot, Flask A, with a thermometer and nitrogen inlet tube was connected through an adapter and condenser to Flasks I to V in series. Flask III contained a standard hydrochloric acid solution through which the nitrogen stream bubbled *via* a capillary tube. A drying tube containing calcium chloride and potassium hydroxide separated Flask III and Flask IV which was immersed in an acetone–Dry Ice bath. Flask V contained a dilute solution of bromine in methylene chloride kept at 0°.

Decomposition. The quaternary ammonium hydroxide solution was concentrated under reduced pressure and placed into Flask A. The excess water was distilled (110–120°) under nitrogen and as the internal temperature rose to 125°, decomposition began and was complete in 1–2 hr. Flask A was heated to 140–185° depending on the compound involved, then allowed to cool to room temperature. Flask IV was weighed and warmed to room temperature under a slow stream of nitrogen while still attached to Flask V. This served to characterize the olefin as the dibromide. Titration of Flask III gave a minimum yield of trimethylamine, which was identified *via* the picrate. In some instances an aliquot of this acidified solution was titrated from unsaturated alcohols.[32] Flask I was chilled and the amine content determined by addition of standard hydrochloric acid followed by back titration. When unsaturated alcohols were present, an aliquot of the acid solution was titrated for olefin.[32] This method of analysis was checked with pure samples of the unsaturated alcohols isolated and shown to be applicable. The acidified solution in Flask I was steam distilled and the neutral materials isolated from the distillate were characterized by physical constants and deriva-

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(29) J. vonBraun, *Ber.*, **49**, 969 (1916).

(30) M. Nakanishi, Japan 8660, *Chem. Abstr.*, **54**, 4391f (1960).

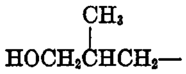
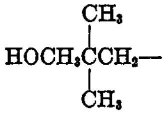
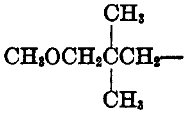
(31) C. Mannich, B. Lesser, and F. Silten, *Ber.*, **65**, 37 (1932).

(32) H. Emde, *Arch. Pharm.*, **247**, 378 (1910).

(33) We wish to thank Dr. E. D. Holley and the Dow Chemical Co. for a generous sample of this resin.

TABLE IV

Methiodides $R\overset{+}{N}(CH_3)_3I^-$

R	Solvent	Crude Yield, %	M.P. Crude	M.P. Anal. sample	% Iodine[a] Calcd.	% Iodine[a] Found
$CH_3CH_2CH_2$—	A	93	187–189	[b]	—	—
 $CH_3\overset{CH_3}{C}HCH_2$—	B	99	227–228	230–231	52.24	52.46
$HOCH_2CH_2CH_2$—	A	98	198–200	201–202	51.78	52.02
 $HOCH_2\overset{CH_3}{C}HCH_2$—	B	92	167–171	172–173	48.98	49.05
 $HOCH_3\underset{CH_3}{\overset{CH_3}{C}}CH_2$—	A	89	223–225	225–226[c]	46.28	46.46
 $CH_3OCH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2$—	A	—	143–145	144–145	44.19	44.30

A. Absolute ethanol. B. Ethanol/ethyl acetate (1:10). [a] Iodine analysis were by the Volhard Procedure. [b] Lit.,[32] m.p. 189°. [c] Lit.,[31] m.p. 226°.

TABLE V

CONDITIONS FOR DECOMPOSITIONS

Method A

Compd.	Mmole.	Dec. Temp.	Time, Hr.	Final[a] Temp.	Total Base Titer,[b] %
III B = OH^-	57.5	125	2	140	97
IV B = OH^-	135	120–130	1.5	160	93
V B = OH^-	129	119–127	1	185	96

Method B

Compd.	Mmole.	t-C_4H_9OH, Mmole.	t-C_4H_9OH, G.	Temp.	Time, Hr.
III B = I^-	134	150	93	81–83	20
IV B = I^-	138	150	99	81–84	46
V B = I^-	141	147	102	78–83	48
V B = I^-	156	173[c]	93[d]	118–123	48
		Method C			
VI B = I^-[e]	94	117	117	79–81	27
VII B = I^-	193	200	148	80–83	34
VII B = I^-	140	148[f]	84[g]	92–95	45
VII B = I^-	111	131[f]	12 + 74[h]	80–82	46

[a] Temperature at conclusion of reaction. [b] The sum of evolved amines and residue in the decomposition flask. [c] Sodium n-pentyl oxide. [d] n-Pentyl alcohol. [e] The condenser used in this reaction was packed with $^1/_{16}$ in. glass helices. [f] Potassium i-butoxide. [g] i-Butyl alcohol. [h] 12 g. i-Butyl alcohol used in the preparation of potassium i-butoxide then diluted with 74 g. t-butyl alcohol.

tives. After the residue from the steam distillation was made basic, any volatile amines were fractionated out by gentle reflux for 24 hr. under a slow stream of nitrogen and were collected in a trap similar to Flask III. The higher boiling amines in Flask I were extracted with ether (continuously), dried, distilled, and identified by physical constants and derivatives. The material remaining in Flask A was worked up similar to Flask I and in some cases combined with Flask I. Material balances (based on amine titer) ranged from 92–97%.

Method B. Decomposition of hydroxyalkyl quaternary ammonium alkoxides. Apparatus. The decomposition train was the same as in Method A with the modification that the condenser was attached to Flask A through a Claisen head.

Decomposition. The alcohols were dried by refluxing with calcium hydride followed by distillation. A mixture of the methiodide and sodium or potassium alkoxide in the corresponding alcohol was refluxed for 20–48 hr. under nitrogen. Flasks I and II were empty and all the volatile amine was trapped in Flask III. The mixture of gaseous olefins and volatile methyl ethers in Flask IV were separated by warming to room temperature and allowing the olefins to distil into Flask V. Flask A was cooled and the potassium iodide was filtered, washed with ether and extracted with hot absolute alcohol or ethyl acetate to recover starting methiodide. The filtrate was diluted with water, the ether and *t*-butyl alcohol were removed by distillation, and the aqueous solution was worked up as described under Method A, Flask I.

Method C. Decomposition of alkyl quaternary ammonium alkoxides. Apparatus. The apparatus differed from Method A in that the condenser was upright and served to fractionate trimethylamine from the medium boiling amines.

Decomposition. The procedure was similar to Method B with reaction time 27–46 hr. One modification in the work-up of Flask A involved distillation of this material into standard hydrochloric acid.

Decompositions. The general conditions for the decompositions are recorded in Table V while the data listing product yields appear in Tables I, II, and III.

Identification of products. 3-Hydroxypropyltrimethylammonium bases. Allyl alcohol, b.p. 96.5°, n_D^{20} 1.4132 (lit.,[34] b.p. 96.9°, n_D^{20} 1.4133) was isolated in 40% yield and characterized as the 3,5-dinitrobenzoate, m.p. 48° (lit.,[35] m.p. 49°); while trimethylamine gave a picrate, m.p. 216–217° (lit.,[36] m.p. 216°) and 3-dimethylaminopropanol-1 was converted to a methiodide, m.p. 197–199°. In the *t*-butoxide decomposition the structure of methyl allyl ether (1%) was based on infrared bands at 6.1 μ, 9.0–9.3 μ and no bands below 3.25 μ.

3-Hydroxyisobutyltrimethylammonium bases. Pure methallyl alcohol, b.p. 112°, n_D^{20} 1.4262 (lit.,[37] b.p. 114°, n_D^{20} 1.4252) was isolated in 6% yield and gave an α-naphthylurethan, m.p. 80–81° (lit.,[38] m.p. 79.6–80.6°). 2-Methyl-3-dimethylammopropanol-1, b.p. 158–160°, n_D^{20} 1.4315 formed a methiodide, m.p. 169–171°. In the *t*-butoxide run a colorless liquid (1.0 g., n_D^{20} 1.3892) collected in Flask IV and based on its infrared spectrum and analysis by refractive index contained methyl methallyl ether (6%) and methyl *t*-butyl ether (2%) (lit.,[39] b.p. 54–55°, n_D^{20} 1.3690). Distillation gave 0.37 g. (3%) of methyl methallyl ether, b.p. 62–64°, n_D^{20} 1.3885 (lit.,[39] b.p. 66.2°, n_D^{20} 1.3943).

Hydroxyneopentyltrimethylammonium bases. Trimethylamine was characterized by both a picrate, m.p. 215–216° and a hydrochloride, m.p. 271° (lit.,[40] m.p. 271–272°). Isobutylene was converted at −75° with bromine in methylene chloride to the dibromide which upon distillation gave the following fractions: I, 5.5 g., b.p. 143–145° (745 mm.), n_D^{20} 1.5084; II, 1.2 g., b.p. 45–46° (16–17 mm.), n_D^{20} 1.5100; III, 1.5 g., b.p. 97–100° (15–16 mm.), n_D^{20} 1.5550 (lit., 2-methyl-1,2-dibromopropane, b.p.[16] 143–145°, $n_D^{21.5}$ 1.5072; 2-methyl-1,2,3-tribromopropane,[16] b.p. 111–114° (22 mm.), $n_D^{21.5}$ 1.5644; b.p.[41] 63–69° (2 mm.), n_D^{20} 1.5650). The yield of isobutylene as determined from the adducts was 30%. Distillation of the high boiling base from Flask I gave: I, 2.0 g., b.p. 138–144°, n_D^{20} 1.4190; II, 2.8 g., b.p. 144–165°, n_D^{20} 1.4260; III, 3.0 g., b.p. 165–168°, n_D^{20} 1.4343. Fraction I was redistilled and gave pure methoxyneopentyldimethylamine, b.p. 138–140°, n_D^{20} 1.4150. An infrared spectrum was identical with an authentic sample and the methiodide, m.p. 144–145° did not depress the melting point of an authentic sample. Fraction III was hydroxyneopentyldimethylamine. Analysis of these fractions involved use of a refractive index-composition curve. In the *t*-butoxide experiment the yield of isobutylene based on distilled bromine adducts was 50% and 2.8 g. (7%) of the starting methiodide, m.p. 220–223°, was recovered. When *n*-pentyl oxide was the base, a 7% yield of methyl *n*-pentyl ether, b.p. 97–100°, n_D^{20} 1.3865 (lit.,[42] b.p. 99–100°, n_D^{10} 1.3855) was isolated and the yield of isobutylene based on distilled bromine adducts was 39%.

n-Propyltrimethylammonium t-butoxide. The amine collected in Flask III gave a picrate, m.p. 211–213.5°[43] (lit.,[36] trimethylamine picrate, m.p. 216°). Propylene was converted to propylene bromide, b.p. 134–138°, n_D^{20} 1.5192–1.5202 (lit.,[44] b.p. 139–142°, n_D^{20} 1.5192); while dimethyl-*n*-propylamine gave a picrate, m.p. 106–108° (lit.,[10] m.p. 108–109°) and a methiodide, m.p. 186–187° (lit.,[32] m.p. 188–189°).

i-Butyltrimethylammonium bases. Trimethylamine was characterized as the picrate, isobutylene as the dibromide, and *i*-butyldimethylamine, b.p. 80–81°, n_D^{20} 1.3915 gave a methiodide, m.p. 228–229°. The ether isolated from the *t*-butoxide run was methyl *t*-butyl ether, b.p. 52–54°, n_D^{20} 1.3698; from *i*-butoxide in *i*-butyl alcohol, methyl *i*-butyl ether, b.p. 57–59°, n_D^{20} 1.3681 (lit.,[45] b.p. 58°); while *i*-butoxide in *t*-butyl alcohol gave a mixture of the above two ethers.

The action of potassium t-butoxide on hydroxyneopentyldimethylamine. A solution of hydroxyneopentyldimethylamine (9.8 g., 75 mmoles), potassium (3.78 g., 96 g.-atoms), and *t*-butyl alcohol (67 g.) was refluxed 4 hr. at 80–89° using the apparatus described under Method B. During this time no volatile amine was trapped in Flask III and no condensate formed in Flask IV. The amino alcohol was recovered in the usual manner and distillation gave 8.5 g. (87%) of hydroxyneopentyldimethylamine, b.p. 68–72° (18 mm.), n_D^{20} 1.4340.

2,2-Dimethyl-3-dimethylamino-1-methoxypropane. Sodium (5.3 g., 0.23 g.-atom), anhydrous toluene (100 ml.) and 2,2-dimethyl-3-dimethylaminopropanol-1 (25.0 g., 0.19 mole) were heated at 100° with stirring for 8 hr. and then dry methyl chloride introduced at 80–100° for 20 hr. After the addition of water (25 ml.) and 40 ml. of concd. hydrochloric acid, the aqueous layer was separated, heated, and made alkaline with sodium hydroxide (30 g., 0.75 mole). The liberated amine was extracted with ether, dried, and upon distillation gave 16.2 g. (59%) of 2,2-dimethyl-3-dimethylamino-1-methoxypropane, b.p. 139–140°, n_D^{20} 1.4155–1.4180. An analytical sample had the following constants: b.p. 140°, n_D^{20} 1.4150.

Anal. Calcd. for $C_8H_{19}NO$: C, 66.15; H, 13.19. Found: C, 66.14; H, 13.15.

NOTRE DAME, IND.

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