

at least as large an amount as the alcohol, II (10% minimum).

(b) From Bicyclo[2,2,2]octene.—Three grams of bicyclo[2,2,2]octene<sup>8</sup> was added to a solution of 3 cc. of water and 6 cc. of concentrated sulfuric acid. The mixture was shaken at 20–25° until homogeneous, diluted with water and steamed. Purification of the distillate by sublimation yielded an alcohol, m.p. 173.4–176.2°, which was identical to that obtained by the above cyclization experiment. The yield of purified alcohol, II, was 73%.

Bicyclo[1,2,3]octane, IV. (a) Via Chloride, III.—A mixture of 0.8 g. of II, 0.6 cc. of dry pyridine, and 3 cc. of pure thionyl chloride was mixed at –80° and sealed into a small tube. After maintaining at 80° for 20 hours, the mixture was poured into ice-water and steamed. The distillate was extracted with ether and this extract washed with bicarbonate, water, and saturated salt solution. The ether was removed by distilling through a column, the last traces under reduced pressure. The residue was sublimed to yield 0.61 g. (66%) of crude solid chloride, III. After three partial sublimations under reduced pressure at 50°, the chloride obtained formed a colorless solid, m.p. 66.6–67.6° in a sealed tube. The chloride is extremely volatile and all operations must be carried out with precautions to avoid loss. It proved difficult to get correct analytical figures as the chloride was always accompanied by oxygenated impurities.

*Anal.* Calcd. for C<sub>8</sub>H<sub>14</sub>Cl: C, 66.4; H, 9.0; Cl, 24.6. Found: C, 65.3; H, 8.9; Cl, 23.2.

In a small flask 0.2 g. of III was dissolved in 8 cc. of ab-

solute alcohol and 0.8 g. of sodium in small pieces was added. The mixture was then refluxed for one hour. It was then diluted with water and steamed into a wide tube within a sublimation tube cooled by a bath held at –80°. The hydrocarbon formed steam distils very rapidly with the first portions of alcohol. The frozen distillate was wiped from the wide tube with cotton and some calcium chloride was added, the whole being pushed down into the sublimation tube. The hydrocarbon was then sublimed onto a cold finger condenser at room temperature. This hydrocarbon is extremely volatile and much was lost in other experiments before adequate precautions were taken. After another sublimation from phosphorus pentoxide a sample of the hydrocarbon, IV, melted at 136.8–137.2° in a sealed tube.<sup>4</sup>

*Anal.* Calcd. for C<sub>8</sub>H<sub>14</sub>: C, 87.3; H, 12.7. Found: C, 87.0; H, 12.8.

(b) Via Ketone, V.—A mixture of 0.2 g. of V, 3 cc. of ethyl mercaptan, 0.12 g. of sodium sulfate and 0.16 g. of freshly fused zinc chloride was held at 5–10° for one day and at 20–25° for 4 hours and then poured into water. The organic product was taken into ether, washed with 10% sodium hydroxide, water, and the ether extract was dried over sodium sulfate. The ether was distilled and the oily residue was refluxed for 15 hours with 20 g. of Raney nickel and 20 cc. of absolute alcohol.<sup>5</sup> The hydrocarbon, IV, was isolated as described above and had the same properties and melting point.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

## The Competitive Formation of Different Olefins from Quaternary Amines

BY PETER A. S. SMITH AND SIMON FRANK<sup>1</sup>

A series of mixed tetraalkylammonium hydroxides has been submitted to the Hofmann degradation. A quantitative comparison of the relative ease of olefin formation has been obtained by mass-spectrometric analysis of the mixtures of olefins produced. Increased branching at the  $\gamma$ -position of an alkyl group successively decreases its conversion to olefin, and in certain cases a statistical effect can be demonstrated.

The decomposition of quaternary ammonium hydroxides on heating to form olefins, water and tertiary amines was described by A. W. Hofmann<sup>2</sup> in 1851 and bears his name. His investigation gave rise to the familiar "Hofmann rule," that ethylene is preferentially formed whenever the quaternary base has an N-attached ethyl group. Since its original formulation, this rule has undergone certain revisions,<sup>3</sup> although it is still substantially valid.

As part of a program of investigation of elimination reactions, Hanhart and Ingold<sup>4</sup> determined the compositions of the mixtures of olefins obtained by the pyrolysis of some quaternary ammonium hydroxides of the type RR'N(CH<sub>3</sub>)<sub>2</sub><sup>+</sup>OH<sup>-</sup>. Their determinations of the proportions of olefins were accomplished by fractional distillation of the olefin dibromides, and led to the generalization that the alkyl group having the most acidic  $\beta$ -hydrogen is preferentially eliminated as olefin. Because of the limitations of the method of analysis then available, the ratios of olefins obtained were only semi-quantitative; in addition, certain not readily ob-

tainable alkyl groups of theoretical interest are not represented in their work.

We have carried out similar experiments on a series of quaternary ammonium hydroxides of the type (R—CH<sub>2</sub>—CH<sub>2</sub>)<sub>2</sub>N<sup>+</sup>(CH<sub>2</sub>—CH<sub>2</sub>—R')<sub>2</sub> OH<sup>-</sup>, and some related types. We were able to determine the ratios of olefins produced with some accuracy, due to the availability of mass-spectrometric analysis, and thus to confirm the results of Hanhart and Ingold. In addition, we were able to extend Hanhart and Ingold's measurements to include the  $\beta$ -*t*-butylethyl group, and to demonstrate the operation of a statistical effect in compounds of the type (R—CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>+<sub>n</sub>N<sup>+</sup>(CH<sub>2</sub>CH<sub>2</sub>—R')<sub>2</sub>-<sub>n</sub>OH<sup>-</sup>.

### Discussion of Results

The quaternary bases examined and the composition of olefins obtained from them are given in Table I. The first three compounds allow a comparison to be made of the relative effect of the groups H-, CH<sub>3</sub>-, CH<sub>3</sub>CH<sub>2</sub>- and (CH<sub>3</sub>)<sub>2</sub>CH-, inasmuch as these groups constitute R and R' in (R—CH<sub>2</sub>—CH<sub>2</sub>)<sub>2</sub>N<sup>+</sup>(CH<sub>2</sub>—CH<sub>2</sub>—R')<sub>2</sub>. It is apparent that the difference between H- and CH<sub>3</sub>- in the  $\beta$ -position is very much greater than the differences among the alkyl groups themselves. Even when a statistical correction is made for the presence of three  $\beta$ -hydrogens in an ethyl group as compared with only two in groups of the type R—CH<sub>2</sub>—CH<sub>2</sub>—

(1) From the doctoral dissertation of Simon Frank, 1950.

(2) A. W. Hofmann, *Phil. Trans.*, **II**, 357 (1851); *Ann.*, **78**, 253 (1851).

(3) For leading references, see E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, New York, N. Y., 1950, Chapter 5; also R. B. Woodward and W. E. Doering, *THIS JOURNAL*, **66**, 849 (1949).

(4) W. Hanhart and C. K. Ingold, *J. Chem. Soc.*, 997 (1927).

TABLE I  
 PROPORTIONS OF OLEFINS FROM QUATERNARY AMINES

Quaternary ammonium hydroxides	Yield of olefins units, %	Percentage found			
		$\text{CH}_2=\text{CH}_2$	$\text{CH}_3-\overset{\text{CH}_2}{\underset{\text{CH}}{\text{C}}}$	$\text{CH}_3-\overset{\text{CH}_2}{\underset{\text{CH}}{\text{C}}}$	$\text{CH}_3-\overset{\text{CH}=\text{CH}_2}{\underset{\text{CH}}{\text{C}}}-\text{CH}_3$ $\text{C}(\text{CH}_3)=\text{CH}_2$
Diethyldi- <i>n</i> -propyl	99	96	4		
Di- <i>n</i> -propyldi- <i>n</i> -butyl	95		63	37	
	97		61	39	
Di- <i>n</i> -butyldi-isoamyl	94			67	33
<i>n</i> -Butylisoamyltrimethyl	83			66	34
Isoamyl- $\beta$ - <i>t</i> -butylethyldimethyl	68				91
Tri- <i>n</i> -propyl- <i>n</i> -butyl	93		83	17	
<i>n</i> -Propyltri- <i>n</i> -butyl	98		36	64	
$\beta$ -Phenylethyltriethyl	0	0			
$\beta$ -Phenylethyltriethyl plus <i>n</i> -propyltrimethyl	79	<1	>99		
Di- <i>n</i> -propyldiisoamyl	94		96		4

there is still a larger difference between H- and  $\text{CH}_3$ - than between homologously adjacent alkyl groups. These statistically corrected ratios should be primarily due to differences in electrical condition in the immediate environment of the  $\beta$ -hydrogen (differences in intrinsic acidity), and to differences in the degree of steric interference with the approach to the  $\beta$ -hydrogen by an attacking hydroxyl group.

The foregoing measurements do not allow these effects to be distinguished sharply, but there are considerations which suggest that steric effects are of minor importance in the compounds discussed above. The bimolecular step wherein steric interference might be encountered presumably involves frontal attack by a hydroxide ion on one of the hydrogen atoms in the  $\beta$ -position. Although alkyl groups exert very significant hindrance of rear-side attack on the carbon atom to which they are attached,<sup>5</sup> they do not appear to be of such a size and situation as to interfere seriously with frontal approach to a hydrogen atom in open-chain compounds. By recourse to molecular scale models, it can be demonstrated that even a *t*-butyl group leaves the hydrogen atoms of a methylene group to which it is attached open to free approach by species considerably larger than hydroxide ion, although the solid angle of free approach is noticeably reduced by the bulk of the *t*-butyl group. For this reason we believe that the relative ease of formation of olefins from groups  $\text{R}-\text{CH}_2-\text{CH}_2-\text{N}^+\equiv$ , as reported here, is a significant index of the relative electrical influences of the groups R, although it is not uninfluenced by steric effects in the extreme cases.

It was desired to include the *t*-butyl group to complete the series of alkyl groups which are being compared. The necessary compound,  $[(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}_2]_2\text{N}^+[\text{CH}_2-\text{CH}_2-\text{C}(\text{CH}_3)_3]_2\text{I}^-$  was prepared only after much disappointing difficulty, and could not be obtained in amounts sufficient for satisfactory investigation. As an alternative, the corresponding dimethyl compound,  $(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2-\text{CH}_2-\text{C}(\text{CH}_3)_3\text{I}^-$ , was found to be obtainable in sufficient quantities. The yield of olefins obtained from this, 68%, indicated that the

side-reaction resulting in alcohol formation<sup>6</sup> was appreciable, which cast some doubt on the reliability of the ratios of olefins obtained from it. To test this point, *n*-butylisoamyltrimethylammonium hydroxide was studied. The olefins, obtained in 83% yield, were formed in the same ratio as from di-*n*-butyldiisoamylammonium hydroxide, which we consider justification for comparing the results from isoamyl  $\beta$ -*t*-butylethyldimethylammonium hydroxide with the results from the non-methylated compounds. As is shown in the fifth entry in Table I, the *t*-butyl group exerts a much greater effect in reducing the ease of olefin formation than do any of the smaller groups. Furthermore, in the introduction of successive methyl groups in the  $\gamma$ -position in going from *n*-propylammonium compounds to  $\beta$ -*t*-butylethylammonium compounds, there is a disproportionately large effect when the third methyl group is added, as compared to the first and second.

The exceptionally strong influence of the *t*-butyl group is also seen in the behavior of alkyltrimethylammonium hydroxides of the type  $\text{R}-\text{CH}_2-\text{CH}_2-\text{N}^+(\text{CH}_3)_3\text{OH}^-$ . The proportion of olefin formed (as opposed to alcohol formation) in this series is given in Table II, compiled from the work of Collie and Schryver,<sup>6</sup> Hanhart and Ingold,<sup>4</sup> and ourselves.

 TABLE II  
 YIELDS OF OLEFINS FROM QUATERNARY AMINES  
 R in  $\text{R}-\text{CH}_2-\text{CH}_2-\text{N}^+(\text{CH}_3)_3\text{OH}^-$     Yield of  $\text{R}-\text{CH}=\text{CH}_2$ , %

H	100 <sup>a</sup>
$\text{CH}_3$	83, 81 <sup>b</sup>
$\text{CH}_3\text{CH}_2$	86, 75 <sup>b</sup>
$(\text{CH}_3)_2\text{CH}$	78
$(\text{CH}_3)_3\text{C}$	20

<sup>a</sup> Ref. 6a.    <sup>b</sup> Ref. 4.

To demonstrate the operation of statistical factors, important in evaluating the behavior of N-attached ethyl groups, the compounds  $(\text{CH}_3-\text{CH}_2-\text{CH}_2)_3\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{OH}^-$  and  $(\text{CH}_3\text{CH}_2\text{CH}_2-\text{CH}_2)_3\text{N}^+\text{CH}_2-\text{CH}_2-\text{CH}_3\text{OH}^-$  were investigated. The ratios of propylene to butylene produced from

(6) (a) N. Collie and S. B. Schryver, *J. Chem. Soc.*, **57**, 767 (1890); (b) J. von Braun, *Ann.*, **382**, 1 (1911); (c) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 526 (1933).

(5) E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

each are reported in Table I. For comparison, predicted ratios for these compounds can be calculated statistically from the experimental result from the intermediate compound, di-*n*-propyl-di-*n*-butylammonium hydroxide. These ratios, 86:14 and 40:60, respectively, agree well with the experimentally found ratios, 83:17 and 36:64, and are taken as affirmative evidence for the existence of a simple statistical effect in these reactions.

It was next felt desirable to relate the properties of the alkyl groups studied directly to that of the phenyl group. Hanhart and Ingold<sup>4</sup> found that the amount of ethylene produced from ethyl- $\beta$ -phenylethyldimethylammonium hydroxide,  $C_6H_5-CH_2-CH_2-NMe_2CH_2CH_3 OH^-$ , was too small to detect, and a numerical comparison of the relative effect of phenyl and hydrogen could not therefore be obtained. We felt that the desired comparison might be obtained by taking advantage of the statistical preference accruing to the ethyl group in  $\beta$ -phenylethyltriethylammonium hydroxide,  $C_6H_5-CH_2CH_2-\overset{+}{N}(CH_2-CH_3)_3 OH^-$ . However, when this compound was decomposed, no weighable amount of ethylene was condensed in the trap for volatile olefins, and only styrene was obtained. Because very small amounts of ethylene could be more surely detected with the use of a known quantity of propylene as a carrier, the experiment was repeated in the presence of *n*-propyltrimethylammonium hydroxide. The weight of volatile olefin collected was 79% of the theoretical quantity of propylene (as compared to 83% when *n*-propyltrimethylammonium hydroxide was decomposed alone), and no ethylene was detectable in it by the mass spectrometer. The difference in electric effect between phenyl and hydrogen must therefore be larger by a different order of magnitude than the difference between hydrogen and methyl, and probably at least as great as the difference between hydrogen and *t*-butyl.

The electric influence of a given alkyl group can be assigned an arbitrary additive value, which will be of useful significance to the extent that this electric influence of an alkyl group remains constant from one compound to another. If hydrogen is given the value 1, after statistical correction for the presence of three  $\beta$ -hydrogens in an ethyl group, then from the ratios of olefins given in Table I the following values can be calculated for the other alkyl groups: methyl, 16; ethyl, 32; isopropyl, 64; *t*-butyl, 640. By use of these figures, the "predicted" ratio of olefins for the decomposition of di-*n*-propyldiisamylammonium hydroxide can be calculated to be 80% propylene: 20% isopentene. The experimentally determined ratio of 96:4 (Table I) is different by so much more than experimental error that one must conclude that structural alterations at the gamma position of one N-attached alkyl group have an unanticipatedly large effect on the  $\beta$ -hydrogens of another alkyl group attached to the same nitrogen. This conclusion is even the less expected in view of the good statistical agreement among the results for the series  $(R-CH_2-CH_2)_{2+n}N^+(CH_2CH_2-R')_2 -OH$ , and it is hoped that we or others may be able to reinvestigate it at a later opportunity.

Numerous attempts at experimental comparison of the electrical properties of alkyl groups have been made. Although there is frequent qualitative agreement between the comparisons variously obtained and the results here reported for olefin formation from quaternary amines, there is no quantitative agreement. This, of course, only indicates the concurrent operation to various extents of factors other than simple transmitted electric effects in most, if not all, experimental approaches to the subject, including the present one. Among the properties which have been measured and compared may be mentioned the ionization constants of acids of the series  $R-COOH$ ,<sup>7</sup>  $R-CH_2-COOH$ , *p*- $R-C_6H_4-COOH$  and *p*- $R-C_6H_4-CH_2COOH$ <sup>8</sup>; the equilibria between hydrocarbons and metal alkyls<sup>9</sup>; the acid strength of alcohols<sup>10</sup>; the basic strengths of primary amines<sup>11</sup>; the dipole moments of monoalkylbenzenes in the vapor phase<sup>8</sup>; the rates of bromination of alkyl benzenes<sup>12</sup>; the rates of reaction of *p*-alkylbenzyl halides with pyridine<sup>13</sup>; the Beckmann rearrangement of aliphatic ketoximes,<sup>14</sup> and the rearrangement of symmetrical *p*-alkylbenzpinacols.<sup>15</sup>

### Experimental

**Tertiary Amines.**—Three of the tertiary amines prepared in the course of this work are new compounds. Each was prepared in essentially the same manner by heating a mixture of 0.27 mole of the symmetrical secondary amine, 0.25 mole of alkyl bromide or iodide, 0.25 mole of anhydrous sodium carbonate and 20 g. of glycerol under reflux with stirring for 48 hours.<sup>16</sup> The oil obtained by subsequent dilution with water was taken up in ether and dried over potassium hydroxide pellets. The crude product obtained by distillation under aspirator vacuum was then treated with benzoyl chloride and sodium acetate followed by alkali to destroy secondary amine. The dried organic layers were then distilled through an eight-inch Vigreux column.

**$\beta$ -*t*-Butylethyl-di-*n*-propylamine** was obtained in 50% yield; b.p. 80–82° (15 mm.),  $n_D^{20}$  1.4275.

*Anal.* Calcd. for  $C_{12}H_{21}N$ : N, 7.57; equiv. wt., 185.4. Found: N (Dumas), 7.70; equiv. wt., 189.

**$\beta$ -*t*-Butylethyl-diisamylamine** was obtained in 44% yield; b.p. 121–122° (15 mm.). Its picrate melted at 77–79°.

*Anal.* Calcd. for  $C_{16}H_{33}N$ : C, 79.60; H, 14.61; equiv. wt., 241.5. Found: C, 79.75; H, 14.25; equiv. wt., 242.5.

***n*-Propyl-diisamylamine** was obtained in 68% yield; b.p. 109–110° (24 mm.). Its methiodide, prepared from the amine and methyl iodide, melted at 142–143°.

*Anal.* Calcd. for  $C_{14}H_{29}NI$ : I, 37.19. Found: I, 36.9.

In addition, two amines whose original preparation<sup>17</sup> has not yet been published were prepared. *n*-Butyldi-*n*-propylamine was obtained in 78% yield, and boiled at

(7) J. F. J. Dippy, *J. Chem. Soc.*, 1222 (1938).

(8) J. W. Baker, J. F. J. Dippy and J. E. Page, *ibid.*, 1774 (1932).

(9) J. B. Conant and G. W. Wheland, *THIS JOURNAL*, **54**, 1212 (1932).

(10) W. K. McEwen, *ibid.*, **58**, 1124 (1936).

(11) G. Bredig, *Z. physik. Chem.*, **13**, 289 (1894); N. F. Hall and M. R. Sprinkle, *THIS JOURNAL*, **54**, 3469 (1932).

(12) E. Berliner and F. Berliner, *ibid.*, **72**, 252 (1950).

(13) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

(14) A. Hantzsch, *Ber.*, **24**, 4018 (1891); A. D. McLaren, *Science*, **103**, 503 (1946).

(15) W. E. Bachmann and F. H. Moser, *THIS JOURNAL*, **54**, 1124 (1932).

(16) S. Caspe, *ibid.*, **54**, 4451 (1932).

(17) John B. Data, Thesis, Univ. of Michigan, 1941—private communication from F. F. Blicke.

TABLE III  
 QUATERNARY AMMONIUM IODIDES PREPARED

Cation	Procedure	M.p., °C.	Recrystn. solvent <sup>a</sup>	Yield, %	Analyses, % I <sup>b</sup>	
					Calcd.	Found
PrNMe <sub>3</sub>	B	192-192.5	E-M	96	55.40	55.29
BuNMe <sub>3</sub>	B	231-232 <sup>o</sup>	E-M	90	52.50	51.78
<i>i</i> -AmNMe <sub>3</sub>	B	203-204	E-K	90	49.35	49.80
<i>t</i> -BuCH <sub>2</sub> CH <sub>2</sub> NMe <sub>3</sub>	B <sup>b</sup>	285 subl.	N	70	46.82	46.81
Et <sub>4</sub> N	A <sup>c</sup>	302	N-M	60	49.35	48.99
Bu <sub>4</sub> N	A	144-145	E-A	80	34.36	34.37
Pr <sub>2</sub> NEt <sub>2</sub>	A <sup>c</sup>	251 dec. <sup>f</sup>	K	70	44.50	44.38
Pr <sub>2</sub> NBu <sub>2</sub>	A	227 dec.	E-K	67	37.18	37.33
BuNPr <sub>3</sub>	A	260 dec.	E-A	60	38.78	38.53
PrNBu <sub>3</sub>	A <sup>c</sup>	198-199	E	50	35.71	35.67
Pr <sub>2</sub> N- <i>i</i> -Am <sub>2</sub>	A	108 dec.	E	50	34.36	34.44
Bu <sub>2</sub> N- <i>i</i> -Am <sub>2</sub>	A	120-120.5	E	63	31.94	31.98
BuNMe <sub>2</sub> - <i>i</i> -Am	A <sup>d</sup>	150-151	E-K	75	42.23	42.41
<i>t</i> -BuCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> - <i>i</i> -Am	A <sup>d</sup>	185-186	W	70	38.78	38.61
PhCH <sub>2</sub> CH <sub>2</sub> NEt <sub>3</sub>	A <sup>d,e</sup>	168-169	W	70	38.18	38.09

<sup>a</sup> E, ethyl acetate (reagent grade); M, methanol (reagent grade); K, acetone; N, acetonitrile; A, ethanol (absolute); W, water. <sup>b</sup> Reaction mixture allowed to stand two weeks in methyl ethyl ketone as solvent. <sup>c</sup> Room temperature for 16 hours. <sup>d</sup> Reaction solvent was acetone. <sup>e</sup> Attempts to prepare quaternary amines from  $\beta$ -phenylethyl bromide and iodide with triethylamine gave largely crude triethylammonium bromide and iodide, respectively. <sup>f</sup> Decomposition temp. depends on rate of heating; K. von Auwers and W. Mauss, *Ber.*, 61, 2420 (1928), report 238-240°. <sup>g</sup> J. von Braun, *Ann.*, 382, 17 (1911), reports 230° dec. <sup>h</sup> Determined by Volhard method.

172-174° (743 mm.) (reported<sup>17</sup> 172-174° (740 mm.)). Isoamyl-di-*n*-butylamine was obtained in 74% yield, and boiled at 107-108° (18 mm.) (reported<sup>17</sup> 96-98° (13 mm.)).

**Quaternary Amines.**—Two general procedures were used, and the results are recorded in Table III. Procedure B was used for the alkyltrimethylammonium iodides, and Procedure A was used for all others, with variations as described in footnotes to the table.

**Procedure A.**—One-tenth mole of the tertiary amine and 0.1 mole of the alkyl iodide (or, occasionally, bromide) were refluxed in 25 ml. of methyl ethyl ketone for 18 hours. The crystalline precipitate which separated on cooling was augmented by the addition of 50 ml. of dry ether, and then filtered and washed with cold methyl ethyl ketone. One recrystallization from ethyl acetate was usually sufficient to give a product whose melting point did not change on further recrystallizations.

**Procedure B.**—To 0.1 mole of the alkyl iodide in a 125-ml. glass stoppered erlenmeyer flask was added 30 ml. of a 25% solution of trimethylamine in absolute methanol. The mixture was then warmed on a steam-bath until the odor of trimethylamine disappeared, and 65 ml. of anhydrous ethyl acetate was added and the mixture heated to boiling. The crystals which separated on cooling were filtered and washed with ethyl acetate. The products were recrystallized from ethyl acetate-methanol mixture, but the melting points were not changed.

**Di- $\beta$ -*t*-butylethyl-diisoamylammonium Iodide.**—Procedure A and several variants of it failed to produce this compound in crystalline state, as did the procedure which

Fuoss and Kraus<sup>18</sup> used to prepare tetraisoamylammonium iodide; the following procedure was the only one of many that were tried to give a product identifiable as the desired product.

A solution of 9.66 g. (0.04 mole) of  $\beta$ -*t*-butyldiisoamylamine and 8.48 g. (0.04 g.) of  $\beta$ -*t*-butylethyl iodide in 50 ml. of methyl isobutyl ketone was heated under reflux on an oil-bath at 140° for 68 hours. A large excess of dry ether was added to the cooled mixture, which then deposited a white, crystalline precipitate; weight 2.5 g. after washing with ether, m.p. 170-180°. This crude product was purified by the method of Fuoss and Kraus,<sup>18</sup> which gave 2.0 g., m.p. 182-182.5°, unchanged on recrystallization from ethyl acetate.

*Anal.* Calcd. for C<sub>22</sub>H<sub>43</sub>NI: I, 27.99. Found: I, 27.55.

**Olefins from Quaternary Amines.**—The quaternary ammonium iodides were first converted to the corresponding hydroxides by treatment with silver oxide, and then pyrolyzed in the apparatus diagrammed in Fig. 1. As all the decompositions were carried out as similarly as possible, it will suffice to describe one experiment as a typical example; the results of all the runs are given in Table IV.

**Di-*n*-butyldiisoamylammonium Hydroxide.**—A solution of 6.0 g. (0.015 mole) of di-*n*-butyldiisoamylammonium iodide in 40 ml. of water and 5 ml. of methanol was shaken for one hour with thoroughly washed silver oxide prepared from 5.1 g. (0.03 mole) of silver nitrate and carbonate-free sodium hydroxide. The filtered solution gave no turbidity with acidified silver nitrate solution; 4.70 ml. of it required 9.70 ml. of 0.1024 *N* hydrochloric acid to phenolphthalein end-point, showing the concentration of the hydroxide to be 0.211 *N*.

**Pyrolysis of Di-*n*-butyldiisoamylammonium Hydroxide.**—The 100-ml. pear-shaped flask at the left end of the apparatus diagrammed in Fig. 1 was charged with 52 ml. (0.0111 mole) of the 0.211 *N* quaternary amine solution prepared as above, and was then fitted with a capillary inlet for nitrogen. The outlet of the flask led through a condenser to the following train: two 125-ml. Drechsel bottles each charged with 20 ml. of 3 *N* hydrochloric acid; a drying tube; a trap immersed in liquid nitrogen, and a mercury bubbler. The drying tube was a U-tube 24 inches long with a capacity of 200 ml.; it was packed with successive layers of soda lime, calcium chloride (8 mesh), crushed Drierite and barium oxide, separated by wads of glass wool.<sup>19</sup> The receiving trap was constructed from a 125-ml. test-tube, and was fitted with a wide-bore inlet tube reaching

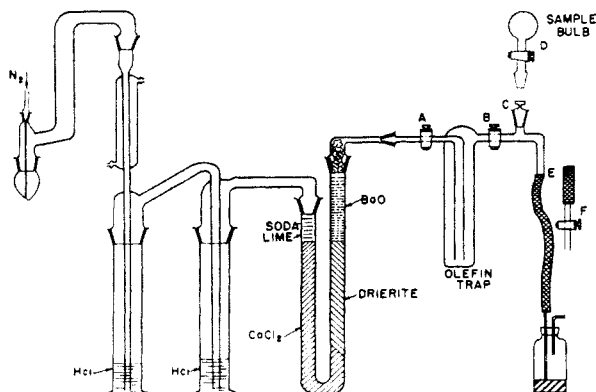


Fig. 1.—Decomposition apparatus.

(18) R. M. Fuoss and C. A. Kraus, *This Journal*, 55, 22 (1933).

(19) J. H. Bower, *Bur. Standards J. Research*, 12, 241 (1934).

TABLE IV  
 PYROLYSIS OF QUATERNARY AMINES

Cation	Equiv. taken	Products		Yield, %
		<i>i</i> -Amine, equiv.	Olefin <sup>a</sup> , g.	
Et <sub>2</sub> NPr <sub>1</sub> <sup>+b</sup>	0.0106	0.0107	0.302	99
Pr <sub>2</sub> NBu <sub>1</sub> <sup>+</sup>	.0110	.0109	.495	95
	.0102	.0096	.472	97
BuNPr <sub>2</sub> <sup>+</sup>	.0119	.0120	.494	93
PrNBu <sub>2</sub> <sup>+</sup>	.0103	.0101	.521	98
Bu <sub>2</sub> N- <i>i</i> -Am <sub>1</sub> <sup>+</sup>	.0111	.0108	.631	94
Pr <sub>2</sub> N- <i>i</i> -Am <sub>1</sub> <sup>+</sup>	.0110	.0110	.448	94
BuMe <sub>2</sub> N- <i>i</i> -Am <sup>+</sup>	.0104	.0103	.522	83
<i>i</i> -BuCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> - <i>i</i> -Am <sup>+</sup>	.0105	.0106	.505	68
PhCH <sub>2</sub> CH <sub>2</sub> NEt <sub>3</sub> <sup>+</sup>	.0055	.0139	.262 <sup>c</sup>	79
PrNMe <sub>3</sub> <sup>+</sup>	.0080			
Et <sub>4</sub> N <sup>+</sup>	.0114	.0113	.310	97
PrNMe <sub>3</sub> <sup>+</sup>	.0102	.0105	.355	83
BuNMe <sub>2</sub> <sup>+</sup>	.0101	.0099	.481	86
Bu <sub>4</sub> N <sup>+</sup>	.0110	.0112	.602	97
<i>i</i> -AmNMe <sub>3</sub> <sup>+</sup>	.0112	.0110	.614	78
<i>i</i> -BuCH <sub>2</sub> CH <sub>2</sub> -NMe <sub>3</sub> <sup>+</sup>	.0151	.0148 <sup>d</sup>	.255	20

<sup>a</sup> See Table I for the composition of the olefin mixtures.

<sup>b</sup> Me = Methyl; Et = ethyl; Pr = *n*-propyl; Bu = *n*-butyl; *i*-Am = isoamyl; Ph = phenyl. <sup>c</sup> A run with  $\beta$ -phenylethyltriethylammonium hydroxide alone gave no weighable amount of volatile olefin. <sup>d</sup> An aliquot of the amine hydrochloride solution was dried to constant weight after repeated evaporations with absolute ethanol. Analysis by Volhard method gave Cl, 23.05%. A 20:80 mixture of the hydrochlorides of Me<sub>3</sub>N and *i*-BuCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (*cf.* Table I) should contain 23.43% Cl.

nearly to the bottom, and with stopcocks at the inlet and outlet. All connections except that to the mercury bubbler were of ground glass.

At the beginning of each run, the apparatus was swept with a stream of nitrogen for 30 minutes. The pear-shaped flask was then immersed in an oil-bath at 85°. The temperature was raised to 175° over 40 minutes, during which time most of the water distilled into the first Drechsel bottle. On raising the temperature to 200°, vigorous decomposition set in, and both amine and olefin distilled into the train. Pyrolysis appeared to be completed in 20 minutes, and only a trace of greyish material remained in the first flask. The train was swept with nitrogen at the

rate of about 80 ml. per minute for 80 minutes longer, whereupon stopcock A was closed and the receiving trap was evacuated to a pressure of 0.05 mm. while still in liquid nitrogen. At this stage the collected olefin was observable as a glass at the bottom of the trap, accompanied by a thin band of moisture or frost at the upper part of the inlet tube. With stopcock B closed, the trap was allowed to come to room temperature and was then weighed against a counterpoise; the increase in weight over that of the evacuated empty trap was 0.634 g. A blank run to determine the amount of moisture collected caused an increase of 0.003 g., giving a net weight of 0.631 g. of olefin, 94% yield as calculated from the composition later determined with the mass spectrometer. Samples for analysis were removed by attaching a sample bulb at the joint C, and evacuating through E attached to the stopcock F. Stopcock F was then closed and B was opened to allow the vaporized olefins to diffuse into the sample bulb. Stopcocks B and D were then closed, and the sample bulb was removed for analysis.

As a check on the material-balance, the combined contents of the two Drechsel bottles were evaporated to a sirup, which was diluted to 50.0 ml. after attempts to obtain crystallization failed. Aliquots of 5.0 ml. were alkalinized and steam distilled in a semimicro Kjeldahl apparatus, the distillate being caught in 25.30 ml. of 0.0999 *N* hydrochloric acid. Back-titration with 0.1024 *N* sodium hydroxide to methyl red end-point required 14.20 ml., indicating the formation of 0.0108 equivalent of volatile amine from the pyrolysis of 0.0111 equivalent of quaternary amine.

The mass spectrometric analyses were carried out by Mr. Worthy T. Boyd of the Department of Chemical Engineering of the University of Michigan using a Consolidated-Nier Isotope-Ratio Mass Spectrometer. To augment and compare with recorded mass spectral data on pure olefins, pure "standards" were prepared in the same manner as the olefin mixtures. The results of these experiments also appear in Table IV. The olefin samples so obtained showed a purity of 98-99% when compared with recorded mass spectrographic data.<sup>20</sup>

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