Acknowledgments.—The authors wish to thank the Colgate Palmolive Co. for the use of their facilities and the Analytical Division of the Research and Development Department for instrumental and microchemical analyses. Thanks are due to Evans Chemetics, Inc., for samples of mercaptoacetic acid and to Armour and Co., Carbide and Carbon Chemicals Corp. and Sharples Chemicals, Inc., for samples of amines.

Brooklyn, New York

[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Amine Oxides. III. Selective Formation of Olefins from Unsymmetrical Amine Oxides and Quaternary Ammonium Hydroxides[1]

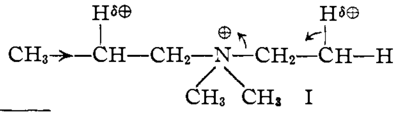
By Arthur C. Cope, Norman A. LeBel,[2] Hiok-Huang Lee[3] and William R. Moore

Received February 6, 1957

The relative amounts of olefins formed in the thermal decomposition of unsymmetrical amine oxides and structurally related quaternary ammonium hydroxides, $R_1R_2MeN^{\oplus}-O^{\ominus}$ and $R_1R_2Me_2N^{\oplus}OH^{\ominus}$, have been determined. The ratios of olefins obtained from the amine oxides are affected less by the structures of the alkyl groups than are the ratios of olefins formed from the quaternary bases, and roughly approximate the ratios of the numbers of β-hydrogen atoms in the alkyl groups. This result is interpreted as being caused by smaller steric effects in the five-membered cyclic transition state for amine oxides than in the planar *trans* transition state leading from quaternary bases to olefins. An order of decreasing ease of elimination of alkyl groups as olefins, corrected for the number of available β-hydrogen atoms, for amine oxides is: β-phenylethyl $\gg$ *t*-butyl > isobutyl $\sim$ isopropyl $\sim$ *n*-decyl > *n*-butyl > isoamyl > ethyl > *n*-propyl. For quaternary ammonium bases the order is β-phenylethyl $\gg$ *t*-butyl > ethyl > isopropyl $\gg$ *n*-propyl > isobutyl $\sim$ *n*-decyl $\sim$ *n*-butyl > isoamyl.

A number of proposals have been advanced to explain the relative amounts of olefins formed in bimolecular elimination reactions. Secondary or tertiary halides undergo elimination to produce the most highly alkylated olefin according to the Saytzeff rule.[4] Hyperconjugative stabilization of the incipient double bond in the transition state leading to the most highly alkylated olefin has been accepted generally as explaining eliminations that proceed by the Saytzeff rule,[5] forming the thermodynamically more stable products.[6]

In the bimolecular eliminations of quaternary ammonium ions (also sulfonium ions), which follow the Hofmann rule,[7,8] other factors must be considered to explain the production of the least highly alkylated, *i.e.*, less stable, olefin. The English workers attribute this directive influence to an inductive effect, brought about by the presence of the unit positive ionic charge in these compounds.[5] The induced positive character of the β-carbon atoms is partially neutralized by an electron-releasing alkyl group (methyl in I, below), causing the β-protons to be less susceptible to attack by base in this alkyl branch. Because of this inductive effect, the terminal methyl group in the *n*-propyl chain (I) acts to suppress propylene formation if elimination can produce ethylene. In support of the above explanation, the relative ease of olefin formation from the decompositions of quaternary ammonium hydroxides has been determined by comparing the yields of olefins from quaternary bases containing only one olefin-yielding alkyl group, and otherwise methyl groups.[8]



$$CH_3\rightarrow\overset{H^{\delta\oplus}}{CH}-CH_2-\underset{CH_3\ \ CH_3}{\overset{\oplus}{N}}-CH_2-\overset{H^{\delta\oplus}}{CH}-H$$

I

A study of the competitive formation of different olefins from a series of quaternary ammonium hydroxides of the type $(RCH_2CH_2)_2N^{\oplus}(CH_2CH_2R')_2$-$OH^{\ominus}$ and some related types has been reported.[9] The observed ratios of olefins formed, statistically corrected for the number of β-hydrogen atoms present, were concluded to be influenced primarily by the electrical properties of the groups R and R′, with steric effects (hindrance to attack by the base) being important only in cases where R or R′ is *t*-butyl.

trans-Stereospecificity has been firmly established for bimolecular elimination reactions[10] if such a reaction course is possible. Steric control of bimolecular elimination reactions of quaternary bases has been proposed by Schramm,[11] who represented the transition states with unlikely configurations. Brown and co-workers, who previously had observed a Hofmann-type elimination in the solvolysis of a tertiary chloride,[12] doubted that the directive influence in elimination reactions following the Hofmann rule necessarily resulted from the presence of a positive charge on the group being eliminated.[13] An increase in the steric requirements (size) of the β-alkyl group or groups,[14a] the base[14b] and the leaving group[14c] has been shown to cause

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[1] Sponsored by the Office of Ordnance Research, U. S. Army, under Contract No. DA-19-020-ORD-3226, Project TB 2-0001(1112).

[2] National Institutes of Health Fellow, 1955–1957.

[3] American Cyanamid Co. Fellow, 1955–1956.

[4] A. Saytzeff, *Ann.*, **179**, 296 (1875).

[5] M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour and G. A. Maw, *J. Chem. Soc.*, 2093 (1948).

[6] For a discussion of the relative stabilities of olefins see G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, This Journal, **57**, 876 (1935); R. S. Mulliken, C. A. Rieke and W. G. Brown, *ibid.*, **63**, 41 (1941).

[7] A. W. Hofmann, *Ann.*, **78**, 253 (1851); **79**, 11 (1851).

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

[9] P. A. S. Smith and S. Frank, This Journal, **74**, 509 (1952).

[10] For leading references see D. J. Cram in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 315–322.

[11] C. H. Schramm, *Science*, **112**, 367 (1950).

[12] H. C. Brown and H. L. Berneis, This Journal, **75**, 10 (1953).

[13] H. C. Brown and I. Moritani, *ibid.*, **78**, 2203 (1956).

[14] (a) H. C. Brown, I. Moritani and M. Nakagawa, *ibid.*, **78**, 2190 (1956); (b) H. C. Brown and I. Moritani, *ibid.*, **78**, 2197 (1956); **75**, 4112 (1953); H. C. Brown, I. Moritani and Y. Okamoto, *ibid.*, **78**, 2193 (1956); (c) H. C. Brown and O. H. Wheeler, *ibid.*, **78**, 2199 (1956).

TABLE I

PROPORTION OF OLEFINS FROM AMINE OXIDES, $R_1R_2MeN^{\oplus}-O^{\ominus}$

R_1	R_2	Yield of olefins, %[a] Ave.	Max.	Composition of olefin mixture in mole %	Statistical ratio, R_2/R_1[d]	Observed ratio, R_2/R_1
s-Butyl	Methyl	91	94	67.3 1-butene, 11.7 *cis*- and 21 *trans*-2-butene	0.667[e]	0.49[e]
3-Pentyl	Methyl	86[b]	88[b]	29.2 *cis*- and 70.8 *trans*-2-pentene	1.0[f]	0.41[f]
Ethyl	*n*-Propyl	82	89	62.5 ethylene, 37.5 propylene	0.667	0.60
Ethyl	Isopropyl	90	91	27.5 ethylene, 72.5 propylene	2.0	2.64
Ethyl	*n*-Butyl	85	88	55.5 ethylene, 44.5 1-butene	0.667	0.80
Ethyl	Isobutyl	85	86	67.6 ethylene, 32.4 isobutylene	0.33	0.48
Ethyl	*t*-Butyl	76	80	14.2 ethylene, 85.8 isobutylene	3.0	6.06
n-Propyl	*n*-Butyl	62	76	43.1 propylene, 56.9 1-butene	1.0	1.32
n-Propyl	Isobutyl	73	86	58.8 propylene, 41.2 isobutylene	0.50	0.70
n-Butyl	Isobutyl	86	88	64.8 1-butene, 35.2 isobutylene	0.50	0.54
n-Propyl	Isoamyl	80	84	44.1[i] propylene, 55.9[i] isoamylene	1.0	1.27
Ethyl	*β*-Phenylethyl	85[c]	90[c]	1.3[g] ethylene	0.667	70.0
n-Propyl	*n*-Decyl	55[c]	62[c]	40.4[h] propylene	1.0	1.47

[a] Over-all yield based on the tertiary amine. [b] The olefins were diluted with a measured volume of nitrogen and the mixture was heated to 45–50° to keep the olefins in the gaseous form. [c] The gaseous component of the olefin mixture was isolated by the procedure used for all of the decompositions, and the liquid olefin was isolated by the procedure described at the end of the Experimental part. [d] Based solely on the numbers of *β*-hydrogen atoms present in R_1 and R_2. [e] Ratio of 2-butene/1-butene. [f] Ratio of *cis*-2-pentene/*trans*-2-pentene. [g] Actual yield of ethylene isolated in per cent. [h] The olefin mixture also contained 59.6% of 1-decene. [i] Percentages showing the relative amounts of propylene and isoamylene. The actual composition of the olefin mixture was 38.7% propylene, 49.1% isoamylene, 11.2% 2-methyl-2-butene and 0.98% of 2-methyl-1-butene.

the elimination reaction to proceed preferentially through the transition state leading to the product that would be predicted by the Hofmann rule (least substituted olefin). All three effects should operate independently and simultaneously. In essence, this explanation states that the greater size of $^{\oplus}NH_3$ groups (and $^{\oplus}SR_2$) compared to halide atoms causes steric effects to become important and diminishes the effect of olefin stability.

In the course of our investigation of the formation of olefins from amine oxides, we have determined the selectivity of olefin formation from the thermal decompositions of unsymmetrical amine oxides of the type $R_1R_2MeN^{\oplus}-O^{\ominus}$ and of the corresponding quaternary ammonium hydroxides $R_1R_2Me_2N^{\oplus}OH^{\ominus}$.

Results

Secondary amines required in this investigation that were prepared by reductive alkylation are listed in Table IV. In Table V are summarized the tertiary amines that were prepared, and their picrates are listed in Table VI. Each of these amines was converted to the corresponding amine oxide by treatment with aqueous hydrogen peroxide. The picrates of the amine oxides, prepared as crystalline derivatives, are listed in Table VII. The methiodides of the tertiary amines were also prepared (Table VIII). Conversion of these salts to the quaternary hydroxides was accomplished either by treatment with silver oxide or with an anion exchange resin.

All of the thermal decompositions were conducted in the apparatus shown in Fig. 1. The total yields of volatile olefins were obtained from volume measurements and were not corrected for deviations from the ideal gas law. The olefin mixtures were analyzed by means of vapor-phase chromatography, employing a thermal conductivity cell as a detecting device. Quantitative results were obtained by graphical integration, as described in the Experimental section. Tables I and II contain a summary of these results. With compounds containing the *β*-phenylethyl and *n*-decyl groups, the liquid olefins were isolated. As a check for reproducibility of both yield and product ratio two to eight pyrolyses were performed on each compound.

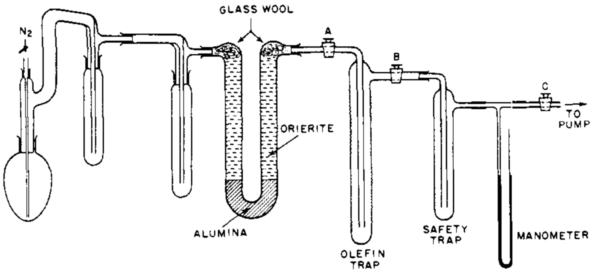


Fig. 1.—Decomposition apparatus.

Tables I and II list product ratios together with statistical ratios, which are the values which would be expected if no directive influence other than the number of *β*-hydrogen atoms available were operative. The significance of this comparison will be illustrated later.

It has been found possible to predict with considerable accuracy product ratios from other amine oxides and quaternary bases containing the olefin-yielding alkyl groups included in our study. For example, from the ratios 1-butene/ethylene (0.80), from methylethyl-*n*-butylamine oxide and propylene/ethylene (0.60), from methylethyl-*n*-propylamine oxide, a predicted value of 1.33 (0.80/0.60) for 1-butene/propylene from decomposition of methyl-*n*-propyl-*n*-butylamine oxide was calculated. The subsequently determined experimental value was 1.32. The fact that product ratios can be predicted in this manner implies that an N-alkyl group either exerts no effect on the ease of elimination of another alkyl group or that it exerts an effect which is additive from one compound to another. This method can be applied to predict the

TABLE II

PROPORTION OF OLEFINS FROM QUATERNARY AMMONIUM HYDROXIDES, $R_1R_2Me_2N^{\oplus}OH^{\ominus}$

1	R_2	Yield of olefins, %[a] Ave.	Max.	Composition of olefin mixture in mole %	Statistical ratio, R_2/R_1[h]	Observed ratio, R_2/R_1
s-Butyl	Methyl	97	97	94.6 1-butene, 3.2 *cis*- and 2.2 *trans*-2-butene	0.667[i]	0.057[i]
3-Pentyl	Methyl	96[b]	98[b]	55.5 *cis*- and 44.5 *trans*-2-pentene	1.0[j]	1.25[j]
Ethyl	*n*-Propyl	94	96	97.6[d] ethylene, 2.4[d] propylene	0.667	0.025
Ethyl	Isopropyl	88	94	41.2 ethylene, 58.8 propylene	2.0	1.43
Ethyl	*n*-Butyl	98	98	98.4 ethylene, 1.6 1-butene	0.667	0.016
Ethyl	Isobutyl	94	95	99.1 ethylene, 0.9 isobutylene	0.33	0.0088
Ethyl	*t*-Butyl	88	91	7.2 ethylene, 92.8 isobutylene	3.0	12.8
n-Propyl	*n*-Butyl	94	94	59.8[e] propylene, 40.2[e] 1-butene	1.0	0.67
n-Propyl	Isobutyl	92	94	72.9 propylene, 27.1 isobutylene	0.50	.37
n-Butyl	Isobutyl	92	92	64 1-butene, 36 isobutylene	0.50	.56
n-Propyl	Isoamyl	95	96	75[f] propylene, 25[f] isoamylene	1.0	.33
Ethyl	β-Phenylethyl	93[c]	93[c]	0.004[g] ethylene	0.667	2.6×10^4
n-Propyl	*n*-Decyl	93[c]	95[c]	59.7[k] propylene	1.0	0.675

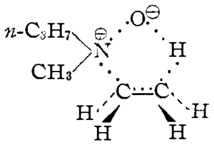
[a] Over-all yield based on the quaternary ammonium iodide. [b] See footnote *b* of Table I. [c] See footnote *c* of Table I. [d] Smith and Frank, ref. 9, report 96% ethylene and 4% propylene from the decomposition of diethyl-di-*n*-propylammonium hydroxide. [e] Smith and Frank, ref. 9, report 63% propylene and 37% 1-butene from decomposition of di-*n*-propyldi-*n*-butylammonium hydroxide. [f] Smith and Frank, ref. 9, report 96% propylene and 4% isoamylene from di-*n*-propyldiisoamylammonium hydroxide. [g] Ref. 9 reports 0% yield of ethylene from the decomposition of β-phenylethyltriethylammonium hydroxide. [h] Based solely on the number of β-hydrogen atoms present in R_1 and R_2. [i] Ratio of 2-butene/1-butene. [j] Ratio of *cis*-2-pentene/*trans*-2-pentene. [k] The olefin mixture also contained 40.3% of 1-decene.

ratios of olefins that will be formed from compounds that have not been studied. For example, the expected value for the ratio isoamylene/1-butene from decomposition of dimethyl-*n*-butylisoamylammonium hydroxide is 0.50. Smith and Frank report this ratio as 0.515 from the above quaternary base and 0.49 from decomposition of di-*n*-butyldiisoamylammonium hydroxide.[9] The values of propylene/ethylene and 1-butene/propylene observed in this work also agree quite well with reported ratios of these olefins obtained from different quaternary bases containing the same alkyl groups.[9] We have found the isoamylene/propylene ratio from dimethyl-*n*-propylisoamylammonium hydroxide to be 0.33, as against a value of 0.042 reported from di-*n*-propyldiisoamylammonium hydroxide.[9] The value in our investigation has been checked repeatedly, and it may be that the previously reported ratio[9] is in error in this case. Some of the empirical ratios that we have calculated are as follows: from amine oxides ($R_1R_2MeN^{\oplus}–O^{\ominus}$); isobutylene (from R = isobutyl)/isoamylene = 0.55; isoamylene/1-butene = 0.96; isoamylene/ethylene = 0.76; from quaternary ammonium hydroxides ($R_1R_2Me_2N^{\oplus}OH^{\ominus}$); isobutylene (from R = isobutyl)/isoamylene = 1.12; isoamylene/ethylene = 0.0082. These calculated ratios are listed to illustrate the utility of the data in predicting the ratios of olefins in thermal decompositions not yet studied.

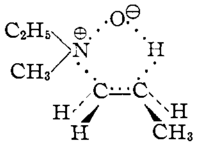
Discussion

The amine oxide decomposition[15] is an elimination reaction which follows predominantly a *cis* steric course.[16,17] In contrast to the bimolecular decomposition of quaternary ammonium hydroxides, this reaction is considered to be an intramolecular elimination similar to the Chugaev reaction[18] and ester pyrolysis.[19] Nevertheless, the amine oxide and quaternary ammonium hydroxide decompositions are alike in some respects. The semi-polar bond between nitrogen and oxygen in an amine oxide causes the nitrogen atom to carry a positive charge, and the "base" is the negatively charged oxygen atom. To the extent that the nitrogen atom of an amine oxide does carry a positive charge, the inductive effect should extend the polarity to the β-carbon atoms of the various alkyl groups. That is, the *relative* acidities of the β-hydrogen atoms should be in the same order for similarly constituted amine oxides and quaternary bases, though the differences would be expected to be smaller in the case of amine oxides. If the acidity of the β-hydrogen atoms is the controlling factor in determining the course of the decompositions of quaternary ammonium ions and amine oxides containing simple alkyl groups, the results of the two reactions should be parallel. However, to the extent that other factors such as the double bond character and hyperconjugative stabilization of the transition state and steric effects determine the course of the elimination, the reactions would be expected to differ.

On the basis of present information, the transition state for the decomposition of an amine oxide can best be described as an essentially planar *quasi* five-membered ring. The transition states that would lead to elimination following the Hofmann rule and the Saytzeff rule can be represented as II and III, respectively.



II, "Hofmann"



III, "Saytzeff"

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(15) A. C. Cope, T. T. Foster and P. H. Towle, THIS JOURNAL, **71**, 3929 (1949).

(16) A. C. Cope, R. A. Pike and C. F. Spencer, *ibid.*, **75**, 3212 (1953).

(17) D. J. Cram and J. E. McCarty, *ibid.*, **76**, 5740 (1954).

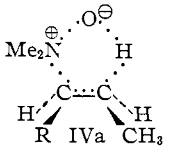
(18) For leading references see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 462.

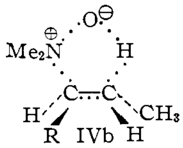
(19) Reference 18, p. 463.

From the data of Tables I and II, it can be seen that the pyrolysis of amine oxides leads to a nearly statistical distribution of olefins, with a slight preference over the statistical ratio for the most highly substituted olefin. This nearly statistical elimination of β-hydrogen atoms may seem surprising in view of the report that the pyrolysis of acetates proceeds in a highly selective manner to give a single olefin following the Hofmann rule.[20] Since the thermal decomposition of acetates and amine oxides involve similar cyclic mechanisms and the amine oxides give substantial amounts of the most highly alkylated olefin, the transition state in the amine oxide decomposition probably has more double bond character than the transition state in the dehydroacetoxylation reaction, allowing more opportunity for hyperconjugative stabilization. Although the propriety of comparing the courses of two elimination reactions that proceed at such widely different temperatures may be questioned, it is quite certain that differences in the degree of C–H bond breaking in the transition states could determine the direction of elimination. Another explanation for the observed differences is concerned with the differences in crowding of groups attached to adjacent atoms in the five- and six-membered cyclic transition states for the pyrolyses of amine oxides and acetates, respectively.

The nearly statistical distribution of olefins suggests that, over-all, the hyperconjugative, inductive and steric effects must essentially cancel. In certain cases the slight deviations from statistical ratios could be rationalized on the basis of a somewhat greater relative importance of one of these effects, but the deviations are so small that no reasonable separation of these effects can be made. However, it is obvious that the inductive effect of a β-alkyl group is not dominant in determining the ratios of olefins formed from amine oxides.

Clearly, all of the steric interactions studied by Brown and his co-workers[13,14] in bimolecular eliminations are not operable in this intramolecular *cis* elimination reaction. Interference of the bulky trisubstituted nitrogen atom with alkyl groups attached to the β-carbon atom is relatively small, regardless of whether elimination is producing the most highly alkylated or least highly alkylated olefin. The type of steric interaction that is present in the five-membered cyclic transition state is concerned with the eclipsing of adjacent groups; *e.g.*, β-alkyl groups with α-hydrogen atoms or alkyl groups and α-alkyl groups with N-alkyl groups.[21] Such non-bonded interactions would be similar to those known to be present in alkylcyclopentanes.[22] The preferential elimination of *t*-butyl and isopropyl groups with respect to the ethyl group shows that the unfavorable eclipsing of the α-methyl groups with the N-alkyl groups does not overcome the hyperconjugative stabilization given by the α-methyl groups. Eclipsing effects alone appear to determine the reaction paths of dimethyl-*sec*-butylamine oxide (IV, R = CH_3) and dimethyl-3-pentylamine oxide (IV, R = C_2H_5). The transition state requires that eclipsing of 1,2-alkyl groups be at a maximum in order to obtain *cis*-olefin (IVa), while production of the *trans* isomer (IVb) would involve only hydrogen–alkyl eclipsing. The *sec*-butyl compound gave 67.3% 1-butene and 11.7% *cis*-, 21% *trans*-2-butene (*cis/trans* = 0.56); the 3-pentyl compound formed 29% *cis*- and 71% *trans*-2-pentene (*cis/trans* = 0.41). These *cis/trans* ratios show that the eclipsing effect may influence the course of the reaction and suggest that the effect is larger when one of the eclipsed groups is ethyl (IVa, R = C_2H_5).


IVa


IVb

The pyrolysis of methyl-*n*-propylisoamylamine oxide gave a volatile olefin mixture which contained two components in addition to the expected propylene and isoamylene. The first of these, which was obtained in 11.2% yield (mole per cent. of the total olefin mixture), was isolated by vapor-phase chromatography. An infrared spectrum of this material in the gaseous phase (under reduced pressure) was identical with the spectrum of 2-methyl-2-butene, and retention times for the olefin and 2-methyl-2-butene in vapor-phase chromatography were the same. The second component, which was present to the extent of 0.98%, showed the same retention time in vapor-phase chromatography as 2-methyl-1-butene and differed from the retention times of the other isoamylenes. The production of these isomeric 2-methylbutenes cannot be attributed to isomerization of isoamylene under the conditions of the reaction, since it has been established that the amine oxide decomposition leads to non-rearranged (*i.e.*, unconjugated) products in systems which are prone to basic isomerization.[23] The possibility that these abnormal products might have arisen from an isomeric impurity in the starting material is excluded by the fact that the olefin formed from the quaternary ammonium hydroxide prepared from the same tertiary amine produced only trace amounts of these isomeric isoamylenes. A possible mechanism that can explain the production of 2-methyl-2-butene is a concerted process in which a γ-hydrogen atom is removed and the formation of a double bond between the β- and γ-carbon atoms is accompanied by a hydride shift from the β- to the α-carbon atom with elimination of dimethylhydroxylamine. An investigation of such abnormal amine oxide elimination reactions is in progress.

In an experiment designed to determine whether the decomposition of an amine oxide was affected by the presence of a strong base, methylethyl-*n*-propylamine oxide was pyrolyzed in the presence of sodium hydroxide. The total yield of olefins was essentially the same as that which was obtained in the absence of sodium hydroxide, and the

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[20] W. J. Bailey and C. King, THIS JOURNAL, **77**, 75 (1955).

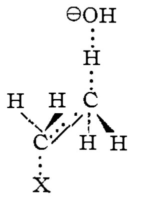
[21] *Cf.* the *cis* effect; D. Y. Curtin, *Record Chem. Progr.* (*Kresge-Hooker Sci. Lib.*), **15**, 111 (1953).

[22] W. Beckett, K. S. Pitzer and K. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

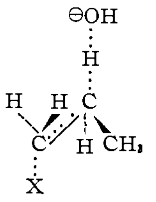
[23] (a) D. J. Cram, *ibid.*, **74**, 2137 (1952); (b) A. C. Cope and C. L. Bumgardner, *ibid.*, **79**, 960 (1957).

ratio of propylene to ethylene was unchanged from the value reported in Table I.

As has been previously observed with quaternary ammonium hydroxides containing an ethyl group and a β-alkylethyl group,[8,9] the pronounced favoring of formation of ethylene over any other olefin is evident from the results in Table II. This preference for ethylene formation could result from the domination of inductive effects[5] or steric effects[13] and indicates that the transition state V is much more favored than VI. Upon consideration of the relative ease of elimination of the ethyl, n-propyl and isobutyl groups, it can be seen that although selective formation of ethylene is highly favored, elimination of an n-propyl group to form propylene is only slightly favored relative to elimination of an isobutyl group. Yet the difference in the inductive effect between n-propyl and isobutyl groups should be equivalent to the difference between ethyl and n-propyl groups. Unless explained by steric effects, the experimental results can be explained only if the hyperconjugative effect becomes abnormally important for production of isobutylene. The statistically corrected[24] isobutylene/ethylene ratio of 4.2, obtained from dimethylethyl-t-butylammonium hydroxide, in which the α-methyl substituents exert a far smaller retarding inductive effect on a β-hydrogen atom,[5] certainly indicates increased hyperconjugative stabilization of the transition state. But the effect appears to be too small to explain the results with the n-propyl and isobutyl groups. An interesting point with regard to the t-butyl compound is that the bulkiness of the groups attached to the α-carbon atom might cause B-strain[25] which would enhance formation of isobutylene. Such an effect would impart some E_1 character to isobutylene formation, allowing for more hyperconjugative stabilization of the transition state than in the normal E_2 elimination. Nevertheless, it is obvious that an inductive effect alone cannot account for the complete domination of ethylene formation.

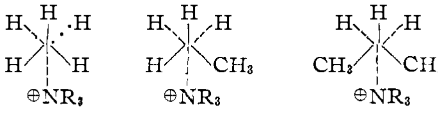


V, X = n-$C_3H_7N^{\oplus}Me_2$, "Hofmann"



VI, X = $C_2H_5N^{\oplus}Me_2$, "Saytzeff"

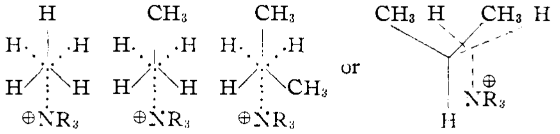
On the other hand, it is possible that there is strong steric control of these reactions by virtue of the interactions of the β-alkyl groups with the extremely bulky leaving group ($^{\oplus}NR_3$) as has been proposed by Brown and co-workers.[13,14] Representing the pertinent transition states for elimination as shown below in the end-on projection formulas VII, it is apparent that the number of β-alkyl . . . $-^{\oplus}NR_3$ interactions are ethyl = 0, n-propyl = 1, isobutyl = 2.



Alkyl group eliminated: Ethyl n-Propyl Isobutyl

VII

When these groups are not being eliminated, *i.e.*, in both the ground state and the transition state leading to elimination of the *other possible* olefin, the number of such interactions should be as represented by VIII, namely, ethyl = 0, propyl = 0, isobutyl $\leq$ 1.



Ethyl n-Propyl Isobutyl

VIII

Thus while the transition state leading to elimination of ethylene involves no increase at all in steric interactions, the transition states leading to elimination of the n-propyl and isobutyl groups both involve an increase of at least one β-methyl . . . $^{\oplus}NR_3$ interaction. That is, this type of steric effect should be quite similar for these two groups.

This suggests that the 27-fold decrease in relative ease of elimination in going from ethyl to n-propyl is due largely to this steric effect and that the much smaller preference (1.4 times) for the elimination of propylene with respect to isobutylene is due to a near cancelling of the inductive and hyperconjugative effects in the absence of further pronounced steric effects.

Such an interpretation of these results would be consistent with the course of the elimination reaction of amine oxides—a reaction which most certainly is *not* controlled by inductive effects when simple alkyl groups are involved. In fact, in the cases studied, the thermal decomposition of quaternary ammonium hydroxides and amine oxides give results which are quite similar except when the quaternary ammonium hydroxide involves a primary β-hydrogen atom competing with a secondary or tertiary β-hydrogen atom. This strongly suggests that the electrical effects are not greatly different in the quaternary ammonium hydroxide and amine oxide decomposition (involving alkyl groups). Large differences in the course of these reactions result only when steric interactions of the type considered above can influence the direction of elimination of quaternary ammonium ions but not amine oxides.

In Table III each of the alkyl groups that we have studied has been assigned an arbitrary value for the relative ease of elimination on the basis of a value of 100 for the ethyl group. This number will be useful as long as the net steric and electrical effects for each group upon the group being eliminated are zero or additive, as they must have been for the compounds included in this study.

The relative ease of elimination is approximately the same when the β-substituent of a quaternary ammonium hydroxide is ethyl (in n-butyl) or n-

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[24] The statistically corrected ratio is the observed ratio/statistical ratio.

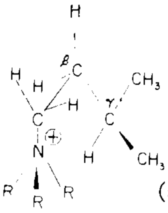
[25] H. C. Brown, *Science*, **103**, 385 (1946).

TABLE III

RELATIVE EASE OF ELIMINATION OF ALKYL GROUPS AS OLEFIN

Alkyl group	Amine oxide Corrected for number of β-hydrogen atoms	Not corrected for number of β-hydrogen atoms	Quaternary ammonium hydroxide Corrected for number of β-hydrogen atoms	Not corrected for number of β-hydrogen atoms
Ethyl	100	100	100	100
Isopropyl	132	264	72	143
t-Butyl	202	606	427	1280
n-Propyl	90	60	3.7	2.45
n-Butyl	120	80	2.4	1.6
Isobutyl	133	44	2.7	0.9
Isoamyl	114	76	1.2	0.8
n-Decyl	132	88	2.5	1.65
β-Phenylethyl	10.5×10^2	7.0×10^2	3.9×10^4	2.6×10^4

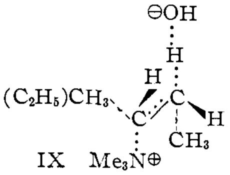
octyl (in *n*-decyl). This result is to be expected since both the steric effect and the inductive effect should be nearly the same for elimination of each group. As is shown by the isoamyl group, branching at the γ-carbon leads to a decrease in the relative ease of elimination.[26] This could be due to a steric effect or an inductive effect[9] or both; however, the corresponding amine oxide shows no inductive control. It seems reasonable, therefore, that the increased steric requirements in the quaternary ammonium hydroxide at least in part cause the decrease in ease of elimination. The larger the group attached to the β-carbon atom is, the more crowding with $-^{\oplus}NR_3$ and the more difficult *trans* elimination of H and $-^{\oplus}NR_3$ becomes. Interaction of a γ-substituent and the $-^{\oplus}NR_3$ group is function of rotation about the C_β–C_γ bond, and for the case (see a) where only two γ-methyl groups are present the important interaction is that of a γ-hydrogen with the leaving group. That is, the increase in "steric hindrance" on going from a β-methylethyl (*n*-propyl) group to a β-isopropylethyl (isoamyl) group involves primarily restriction of rotation about the C_β–C_γ bond. But when three γ-methyl groups are involved (*i.e.*, the β-alkyl group is *t*-butyl), there must be direct $^{\oplus}NR_3$. . . γ-methyl interactions in the transition state and the observed[9] drastic decrease in the relative ease of elimination of the β-*t*-butylethyl group is not surprising.



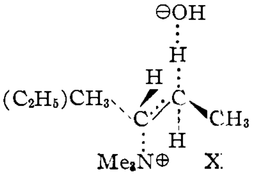
(a)

Pyrolysis of trimethyl-*sec*-butylammonium hydroxide led to a ratio of 1-butene/2-butene = 17.7. On the other hand, the ethoxide-induced bimolecular elimination of dimethyl-*sec*-butylsulfonium ion gave a ratio of 2.9.[27] Evidence has been presented that the strength of the base does not play a major role in altering the isomer distribution in E_2 eliminations.[14a] The large difference in the direction of elimination of these two ions must be due to steric and/or electrical effects. Inductive effects in the two ions should be the same since both are unipositive and the *meta* sigma values for the trimethylammonium and dimethylsulfonium groups are nearly identical.[28] It would seem, therefore, that this large difference is due mainly to steric effects. However, the increase in the amount of 1-olefin obtained from the ammonium ion relative to the sulfonium ion does not necessarily result *solely* from steric effects (size of the leaving group) as previously concluded.[14c] Sulfonium ions can undergo E_1 elimination, *i.e.*, the leaving group is more readily eliminated than the leaving group in quaternary ammonium bases. To the extent that this tendency for bond breaking becomes more important in the transition state for E_2 elimination, a sulfonium ion would be expected to give a larger proportion of the more stable olefin.

Bimolecular eliminations from the 2-pentyl system (bromide, iodide, tosylate, dimethyl sulfone and dimethylsulfonium ion) led to a larger amount of *trans*- than *cis*-2-pentene.[14c] Elimination from the dimethyl-*sec*-butylsulfonium ion has been reported to give mostly *trans* isomer in the 2-butene fraction.[27] The relative amounts of *cis–trans* isomers reflect the relative magnitudes of the eclipsing of 1,2-alkyl groups in the transition states leading to the isomeric olefins. Thermal decomposition of trimethyl-*sec*-butylammonium hydroxide and trimethyl-3-pentylammonium hydroxide gave *cis*/*trans* isomer ratios of 1.41 and 1.25, respectively. To the extent that the transition states leading to the *cis* isomer IX and to the *trans*-isomer X resemble the starting materials,[29] it is reasonable that the eclipsing effects demonstrated in the corresponding amine oxides are diminished. The slight preference for the *cis* isomers indicates that eclipsing of the 1,2-alkyl groups (methyl or ethyl) did not determine the course of the reaction and that some other internal steric effects must account for these results.



IX



X

Pyrolysis of methylethyl-β-phenylethylamine oxide gave a styrene/ethylene ratio of 70, whereas the corresponding quaternary ammonium hydroxide gave a ratio of 27,000. The marked preference for styrene in these cases must be primarily due to the

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(26) See also ref. 9.

(27) E. D. Hughes, C. K. Ingold, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2077 (1948).

(28) F. G. Bordwell and P. J. Boutan, THIS JOURNAL, 78, 87 (1956).

(29) D. J. Cram, F. D. Greene and C. H. Depuy, *ibid.*, **78**, **790** (1956), in their study of bimolecular eliminations of the diastereoisomeric 1,2-diphenyl-1-propyltrimethylammonium ions with ethoxide have presented evidence for the resemblance of the transition states to the olefinic products. However, their compounds would involve far more conjugative stabilization of the transition states and would be expected to differ from the simpler cases included in our study. Nonconcerted eliminations involving prior formation of a carbanion are excluded since the more stable *trans* isomers would be expected as the major products.

increased acidity of the β-hydrogen atom and to the great conjugative stabilization of the forming double bond by the phenyl group. In both cases the double bond character of the transition state is probably greater than when simple alkyl groups are involved. In view of the fact that styrene formation relative to ethylene formation was approximately 390 times faster with the quaternary ammonium hydroxide than with the amine oxide, the implication is that the double bond character of the transition state must be greater for the decomposition of the quaternary ammonium hydroxide than for the amine oxide. This conclusion may well extend to a comparison of the two reactions in general. Previous work also shows the tendency for the amine oxide decomposition to give conjugated olefins preferentially.[17,23b]

Experimental[30]

Secondary Amines.—Each of the secondary amines listed in Table IV was prepared by the reductive alkylation of a primary amine with the appropriate carbonyl compound. The general procedure adopted is illustrated by the preparation of *n*-butylisobutylamine.

A suspension of 0.55 g. of platinum oxide in 200 ml. of absolute ethanol was shaken with hydrogen in a 1-l. pressure bottle until no more hydrogen was absorbed. *n*-Butylamine (72 g., 0.99 mole) then was added to the catalyst mixture followed by a solution of 65 g. (0.90 mole) of isobutyraldehyde in 100 ml. of absolute ethanol, which was added slowly and with cooling. The mixture was shaken with hydrogen at an initial pressure of 30 p.s.i. for 110 min., by which time the theoretical amount of hydrogen was absorbed. The catalyst was separated by filtration, washed with ethanol, and 80 ml. of concentrated hydrochloric acid was added to the combined filtrates. The solution was then concentrated to dryness under reduced pressure (15–20 mm.). The solid residue was dissolved in 250 ml. of water, and 160 g. of 50% sodium hydroxide was added slowly with cooling to liberate the amine. The mixture was extracted with three 200-ml. portions of ether and the ether solutions were dried over potassium hydroxide and concentrated. The residue was distilled through a 46 × 1.5-cm. spinning-band column, yielding 106.7 g. (92%) of *n*-butylisobutylamine, b.p. 80.5–81.5° (80 mm.), $n^{25}D$ 1.4103.

Ethyl-*t*-Butylamine.—N-*t*-Butylacetamide was prepared in 73% yield by adding acetic anhydride to a solution of *t*-butylamine in 10% aqueous sodium hydroxide at 0° followed by heating the mixture at 50–60° for 1.5 hr. and extracting continuously with chloroform for 18 hr. The amide melted at 98–99° (lit.[31] m.p. 97–98°) after one recrystallization from hexane. Reduction of the amide in tetrahydrofuran solution with lithium aluminum hydride according to the procedure of Moffett[32] gave a 60% yield of ethyl-*t*-butylamine, b.p. 85–87°, $n^{25}D$ 1.3936, d_4^{25} 0.7161.

Anal. Calcd. for $C_6H_{15}N$: C, 71.21; H, 14.94; N, 13.84. Found: C, 70.99; H, 14.75; N, 13.95.

Ethyl-β-phenylethylamine.—Ethyl-β-phenylethylamine was prepared in 47% yield according to the procedure of Blicke and Monroe[33] from β-phenylethyl bromide and ethylamine. The product, b.p. 102° (15 mm.), formed a hydrochloride, m.p. 183–184° (lit.[33] m.p. 181–182°).

Tertiary Amines.—The tertiary amines, with the exceptions of N,N-dimethyl-*sec*-butylamine and methyl-*n*-propyl-*n*-decylamine, were prepared by methylating the secondary amines described above with formic acid and formaldehyde according to the procedure of Icke and Wisegarver.[34] The yields of the tertiary amines are recorded in Table V. The picrates of the amines are listed in Table VI.

Methyl-*n*-propyl-*n*-decylamine.—To a solution of 79 g. (0.5 mole) of *n*-decyl alcohol in 158 g. (2.0 moles) of pyridine at 0° was added 105 g. (0.55 mole) of *p*-toluenesulfonyl chloride. The mixture was allowed to remain at 6–12° for 5 hr., then poured into 1 l. of 30% hydrochloric acid at 0°. The acid mixture was extracted with three 200-ml. portions of ether; the ether solutions were dried and concentrated. The sirupy residue was dissolved in 250 ml. of benzene, cooled, and 86 g. (1.2 moles) of methyl-*n*-propylamine was added. The solution was allowed to stand at room temperature for 40 hr., then dissolved in 500 ml. of ether, and the ether solution was extracted with two 250-ml. portions of 10% hydrochloric acid. The acid solution was cooled and made strongly alkaline with sodium hydroxide. The liberated amine was extracted with three 200-ml. portions of ether; the ether extracts were dried over potassium hydroxide pellets and concentrated. Distillation of the residue through a 46 × 1.5-cm. spinning-band column gave 76.4 g. (72%) of methyl-*n*-propyl-*n*-decylamine, b.p. 89–90° (1 mm.), $n^{25}D$ 1.4340.

Quaternary Ammonium Iodides.—The quaternary salts were prepared by refluxing a mixture of the tertiary amine and excess methyl iodide in ether or benzene solution on a steam-bath for 1–3 hr. The yields and melting points of the methiodides are listed in Table VII.

Amine Oxides.—The tertiary amines were oxidized with 30% aqueous hydrogen peroxide in methanol solution, and the excess hydrogen peroxide was decomposed by adding platinum black by essentially the procedure described for preparing N,N-dimethylcyclooöctylamine oxide.[16] The scale of oxidation was limited to 0.01 mole of tertiary amine, and the amine oxide solution was used directly for pyrolysis after removing the platinum black by filtration. The yields of the amine oxides were determined from separate preparations by converting them to the crystalline picrates which are listed in Table VIII.

Quaternary Ammonium Hydroxides.—The quaternary ammonium iodides were converted to the corresponding hydroxides by dissolving 0.01 mole of the salt in 10–15 ml. of water and passing the solution over an ion-exchange column (Amberlite IRA-400, basic cycle) or stirring the solution with a 100% excess of silver oxide (U.S.P.) for 2–3 hr. at 0° and removing the excess silver oxide and silver iodide by filtration. The two methods appeared to give equally good results.

Pyrolysis of Amine Oxides and Quaternary Bases.—A solution of 0.01 mole of the amine oxide or quaternary base prepared as above was concentrated at room temperature under reduced pressure (0.1 mm.) in a 100-ml. pear-shaped flask to a sirupy residue (*ca.* 2 ml.). The flask was then connected to the decomposition apparatus in the manner shown in Fig. 1 and fitted with a capillary inlet for nitrogen. The outlet of the flask led to the following train: two 15 × 2-cm. tubes each cooled to −20° in order to freeze out water or dialkylhydroxylamines formed from the decomposition; a U-tube of 150-ml. capacity, which was packed with 40 g. of 8–20 mesh activated alumina in the bottom and crushed Drierite in both arms; and finally two traps immersed in liquid nitrogen. The section of the U-tube containing the alumina was cooled to −70° during the decomposition in order to absorb completely the gaseous olefins produced. After decomposition was complete, the olefins were eluted at higher temperatures from the alumina by nitrogen and isolated in the olefin trap cooled with liquid nitrogen. Fresh alumina and Drierite were used for each decomposition. The olefin trap was constructed from a 31 × 2.5-cm. Pyrex tube and had a wide-bore (1 cm.) inlet tube reaching nearly to the bottom and a series of indentions around the outer wall to effect better cooling. It was fitted with stopcocks (A and B) at the inlet and outlet and its volume was accurately determined. The second trap, also immersed in liquid nitrogen, was of simpler construction as shown in Fig. 1. It was used as a safety trap to prevent accidental entrance of air and moisture into the olefin trap. All connections except that to the manometer and vacuum source were of ground glass.

Before actual decomposition of the amide oxide or quaternary base was attempted, known volumes of standard samples[35] of ethylene, 1-butene, isobutylene and isoamylene were passed into the apparatus and then isolated under the

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[30] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

[31] J. J. Ritter and P. P. Minieri, THIS JOURNAL, **70**, 4045 (1948).

[32] R. B. Moffett, *Org. Syntheses*, **33**, 33 (1953).

[33] F. F. Blicke and E. Monroe, THIS JOURNAL, **61**, 91 (1939).

[34] "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 723.

[35] Obtained from the Phillips Petroleum Co.; minimum purity 99%.

TABLE IV

SECONDARY AMINES, R_1R_2NH, PREPARED BY REDUCTIVE ALKYLATION

R_1	R_2	Source: Carbonyl compound	Source: Primary amine	Yield, %	B.p., °C. (mm.)	$n^{25}D$
Methyl	*n*-Propyl	Propionaldehyde	Methyl	25	61–62.5	1.3858[a]
Ethyl	*n*-Propyl	Propionaldehyde	Ethyl	51	69.5–71	1.3861[b]
Ethyl	Isopropyl	Acetone	Ethyl	64	81–83	1.3936[c]
3-Pentyl	Methyl	Diethyl ketone	Methyl	50	104	1.4060
Ethyl	*n*-Butyl	Butyraldehyde	Ethyl	44	64–65 (130)	1.4035[e]
Ethyl	Isobutyl	Isobutyraldehyde	Ethyl	22	97–98	1.3985[d]
n-Propyl	*n*-Butyl	Butyraldehyde	Propyl	69	73–74 (92)	1.4090[b]
n-Propyl	Isobutyl	Isobutyraldehyde	Propyl	80	123–125	1.4043[b]
n-Butyl	Isobutyl	Isobutyraldehyde	Butyl	92	80.5–81.5 (80)	1.4103[e]
n-Propyl	Isoamyl	Isovaleraldehyde	Propyl	72	148–149	1.4140[b]

[a] Previously reported by J. v. Braun, F. Jostes and H. Wagner, *Ber.*, 61, 1423 (1928). [b] Previously reported by K. N. Campbell, A. H. Sommers and B. K. Campbell, THIS JOURNAL, 66, 82 (1944). [c] H. C. Brill, *ibid.*, **54**, 2484 (1932). [d] W. Marckwald and A. F. v. Droste-Huelshoff, *Ber.*, **32**, 560 (1899). [e] H. R. Henze and D. D. Humphreys, THIS JOURNAL, **64**, 2878 (1942).

TABLE V

N-METHYL TERTIARY AMINES, R_1R_2NMe

R_1	R_2	Yield, %	B.p., °C. (mm.)	$n^{25}D$	d^{25}_4	Formula	*MR* Calcd.	*MR* Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
s-Butyl	Methyl	25[a]	93–93.5	1.4000	0.7340	$C_6H_{15}N$	33.86	33.41	71.21	71.19	14.94	14.96	13.84	13.82
3-Pentyl	Methyl	84	116–117	1.4080	.7507	$C_7H_{17}N$	38.48	38.25	72.96	73.08	14.88	14.86	12.16	11.87
Ethyl	*n*-Propyl	56	91–92[b]	1.3952	.7180	$C_6H_{15}N$	33.86	33.80						
Ethyl	Isopropyl	72	91–92	1.3981	.7214	$C_6H_{15}N$	33.86	33.86	71.21	71.54	14.94	14.84	13.84	13.71
Ethyl	*n*-Butyl	72	117	1.4048	.7320	$C_7H_{17}N$	38.48	38.56	72.96	73.11	14.88	15.10	12.16	12.36
Ethyl	Isobutyl	62	106–107[c]	1.3990	.7293	$C_7H_{17}N$	38.48	38.22						
Ethyl	*t*-Butyl	60	110	1.4088	.7444	$C_7H_{17}N$	38.48	38.25	72.96	72.85	14.88	14.81	12.16	12.41
n-Propyl	*n*-Butyl	73	138	1.4102	.7420	$C_8H_{19}N$	43.10	43.32	74.34	74.36	14.82	14.88	10.84	10.66
n-Propyl	Isobutyl	88	128–130	1.4047	.7327	$C_8H_{19}N$	43.10	43.18	74.34	74.17	14.82	14.72	10.84	10.97
n-Butyl	Isobutyl	97	81–81.3 (75)	1.4109	.7432	$C_9H_{21}N$	47.72	47.87	75.45	75.36	14.77	14.98	9.78	10.03
n-Propyl	Isoamyl	87	153	1.4140	.7513	$C_9H_{21}N$	47.72	47.53	75.45	75.76	14.77	14.63	9.78	9.60
Ethyl	β-Phenylethyl	92	106 (15)	1.4975	.8893	$C_{11}H_{17}N$	53.35	53.91	80.92	80.90	10.50	10.58	8.58	8.78
n-Propyl	*n*-Decyl	72	89–90 (1)	1.4340	.7808	$C_{14}H_{31}N$	71.00	71.18	78.79	78.67	14.64	14.61	6.56	6.64

[a] Prepared by hydrogenating a mixture of methyl ethyl ketone and dimethylamine in ethanol over platinum oxide. [b] J. Meisenheimer and H. Bernhard, *Ann.*, **428**, 252 (1922), report b.p. 91–92°. [c] W. Marckwald and A. F. v. Droste-Huelshoff, *Ber.*, **32**, 560 (1899), report b.p. 105°.

TABLE VI

N-METHYL TERTIARY AMINE PICRATES

R_1	R_2	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
s-Butyl	Methyl	197–198 d.[a]	$C_{12}H_{18}N_4O_7$	43.63	43.80	5.49	5.81	16.96	16.82
3-Pentyl	Methyl	180.5–182.5[b]	$C_{13}H_{20}N_4O_7$	45.34	45.52	5.85	5.87	16.27	16.06
Ethyl	*n*-Propyl	94.4–95.2[c]							
Ethyl	Isopropyl	208–208.7[a]	$C_{12}H_{18}N_4O_7$	43.63	43.64	5.49	5.71	16.96	16.98
Ethyl	*n*-Butyl	77.4–78.4[b]	$C_{13}H_{20}N_4O_7$	45.34	45.53	5.86	5.64	16.27	16.17
Ethyl	Isobutyl	97–98[b]	$C_{13}H_{20}N_4O_7$	45.34	45.05	5.86	6.04	16.27	16.54
Ethyl	*t*-Butyl	239.5–241 d.[b]	$C_{13}H_{20}N_4O_7$	45.34	45.38	5.86	5.92	16.27	16.38
n-Propyl	*n*-Butyl	69.2–70.2[b]	$C_{14}H_{22}N_4O_7$	46.92	46.85	6.19	6.29	15.64	15.49
n-Propyl	Isobutyl	100.3–101.8[b]	$C_{14}H_{22}N_4O_7$	46.92	47.08	6.19	6.25	15.64	15.83
n-Butyl	Isobutyl	51–54[d]	$C_{15}H_{24}N_4O_7$	48.38	48.22	6.50	6.58	15.05	15.12
n-Propyl	Isoamyl	96–97[b]	$C_{15}H_{24}N_4O_7$	48.38	48.73	6.50	6.59	15.05	15.09
Ethyl	β-Phenylethyl	118.4–119.4[b]	$C_{17}H_{20}N_4O_7$	52.04	52.01	5.14	5.45	14.28	14.47
n-Propyl	*n*-Decyl	Oil[e]							

[a] Recrystallized from absolute ethanol. [b] Recrystallized from aqueous methanol. [c] J. Meisenheimer and H. Bernhard, *Ann.*, **428**, 252 (1922), report m.p. 94–95°. [d] Recrystallized from a mixture of methanol and ether. [e] Hydrogen oxalate, recrystallized from dry ethyl acetate, has m.p. 108.8–109.8°. Calcd. for $C_{16}H_{33}NO_4$: C, 63.33; H, 10.96; N, 4.62. Found: C, 62.97; H, 11.04; N, 4.54.

conditions of the amine oxide and Hofmann decompositions. In each case, a 96–98% recovery of the olefin was obtained and the purity of the recovered olefin was determined by vapor-phase chromatography (described below).

At the beginning of each decomposition, the first two tubes were cooled to −20° and the apparatus (containing an atmosphere of nitrogen) was evacuated to 15–20 mm. pressure. The safety trap was immersed in liquid nitrogen, then the alumina was cooled to −70° and finally the olefin trap was cooled with liquid nitrogen. The pear-shaped flask was then immersed in an oil-bath at 85°, and the temperature was raised at the rate of 4° per minute to 150°, by which time decomposition and distillation of the products into the train were complete. The stopcock C was then closed and the system was equilibrated under nitrogen to atmospheric pressure (as indicated by the manometer). The first two tubes and the alumina were allowed to warm to room temperature and the train was eluted with nitrogen at a rate of 10–12 ml. per min. for 1 hr. The alumina was then heated to 90–95° in an oil-bath in a period of 0.5 hr., and elution with nitrogen was continued at this temperature for 4–6 hr., after which stopcocks A and B were closed and the olefin trap was removed and connected to a gasometer (Fig. 2). The gasometer and the olefin trap, which was

TABLE VII

N,N-DIMETHYL QUATERNARY AMMONIUM IODIDES, $R_1R_2NMe_2I$

R_1	R_2	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Iodine, % Calcd.	Iodine, % Found
s-Butyl	Methyl	87	258–259[b]	$C_7H_{18}NI$	34.58	34.61	7.46	7.36	5.76	6.02		
3-Pentyl	Methyl	95	233.3–234 d.[b]	$C_8H_{20}NI$	37.36	37.52	7.84	7.71			49.35	49.43
Ethyl	*n*-Propyl	90[a]		$C_7H_{18}NI$								
Ethyl	Isopropyl	99	268–269 d.[c]	$C_7H_{18}NI$	34.58	34.71	7.46	7.34			52.20	51.92
Ethyl	*n*-Butyl	89	195–195.5[b]	$C_8H_{20}NI$	37.36	37.28	7.84	7.95	5.45	5.77		
Ethyl	Isobutyl	93	184–185[b]	$C_8H_{20}NI$	37.36	37.63	7.84	7.74	5.45	5.28		
Ethyl	*t*-Butyl	93	212.7–213.6 d.[c]	$C_8H_{20}NI$	37.36	37.36	7.84	7.79			49.35	49.25
n-Propyl	*n*-Butyl	94	189–189.4[b]	$C_9H_{22}NI$	39.86	39.69	8.18	8.02	5.17	5.18		
n-Propyl	Isobutyl	82	194–194.6[b]	$C_9H_{22}NI$	39.86	39.98	8.18	8.08	5.17	5.34		
n-Butyl	Isobutyl	98	177.6–178.4[d]	$C_{10}H_{24}NI$	42.11	42.35	8.48	8.41			44.50	44.23
n-Propyl	Isoamyl	95	148–148.8[b]	$C_{10}H_{24}NI$	42.11	42.19	8.48	8.44	4.91	4.87		
Ethyl	β-Phenylethyl	93	145.2–146.2[b]	$C_{12}H_{20}NI$	47.22	47.38	6.61	6.69	4.59	4.43		
n-Propyl	*n*-Decyl	84	56–57.3[e]	$C_{15}H_{34}NI$	50.70	50.70	9.64	9.43			35.71	35.90

[a] The quaternary ammonium iodide was very hygroscopic. The quaternary ammonium picrate was prepared and melted at 183.4–184.4°. W. Hanhart and C. K. Ingold, *J. Chem. Soc.*, 997 (1927), report m.p. 185–187°. [b] Recrystallized from a mixture of absolute ethanol and dry ether. [c] Recrystallized from absolute ethanol. [d] Recrystallized from acetone. [e] Recrystallized from a mixture of dry ethyl acetate and ether.

TABLE VIII

DIALKYLMETHYLAMINE OXIDES, $R_1R_2MeN^+–O^-$

		Picrate								
R_1	R_2	Yield,[a] %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
s-Butyl	Methyl	99	166.8–167.5[b]	$C_{12}H_{18}N_4O_8$	41.62	41.56	5.24	5.49	16.18	16.47
3-Pentyl	Methyl	99	148.6–149.6[c]	$C_{13}H_{20}N_4O_8$	43.33	43.58	5.60	5.80	15.55	15.65
Ethyl	*n*-Propyl	82	104.5–105.3[d]	$C_{12}H_{18}N_4O_8$						
Ethyl	Isopropyl	85	190.5–192 d.[e]	$C_{12}H_{18}N_4O_8$	41.62	41.72	5.24	5.29	16.18	16.10
Ethyl	*n*-Butyl	84	90.4–91[c]	$C_{13}H_{20}N_4O_8$	43.33	43.58	5.60	5.72	15.55	15.51
Ethyl	Isobutyl	85	113–113.8[f]	$C_{13}H_{20}N_4O_8$	43.33	43.30	5.60	5.82	15.55	15.46
Ethyl	*t*-Butyl	83	179.2–180.2 d.[c]	$C_{13}H_{20}H_4O_8$	43.33	43.53	5.60	5.90	15.55	15.60
n-Propyl	*n*-Butyl	90	65.2–66.2[f]	$C_{14}H_{22}N_4O_8$	44.92	44.98	5.92	6.08	14.97	15.05
n-Propyl	Isobutyl	90	86–86.6[f]	$C_{14}H_{22}N_4O_8$	44.92	45.19	5.92	6.08	14.97	14.92
n-Butyl	Isobutyl	91	69–71[g]	$C_{15}H_{24}N_4O_8$	46.39	46.66	6.23	6.48	14.42	14.64
n-Propyl	Isoamyl	90	91.2–92.2[f]	$C_{15}H_{24}N_4O_8$	46.39	46.62	6.23	6.36	14.43	14.70
Ethyl	β-Phenylethyl	97	119.2–119.8[f]	$C_{17}H_{20}N_4O_8$	50.00	50.16	4.94	5.25	13.72	13.69
n-Propyl	*n*-Decyl		Oil							

[a] Over-all yield based on the tertiary amine. [b] Recrystallized from absolute ethanol. [c] Recrystallized from benzene. [d] Recrystallized from absolute methanol. J. Meisenheimer and H. Bernhard, *Ann.*, **428**, 254 (1922), report m.p. 106–107°. [e] Recrystallized from ethyl acetate. [f] Recrystallized from aqueous ethanol. [g] Recrystallized from a mixture of methanol and ether.

still immersed in liquid nitrogen, were evacuated through stopcocks B and E to a pressure of 0.05 mm. With stopcock E closed to the vacuum source, the trap was allowed to come to room temperature, whereupon the glassy olefins vaporized into the gasometer. Using a total volume consisting of the pre-determined volume of the trap and the observed volume in the gasometer, the yield of olefins from the decomposition was then calculated by the ideal gas law. Table I lists the yields of olefins from amine oxide decompositions and Table II lists the yields of olefins from the decompositions of the quaternary bases.

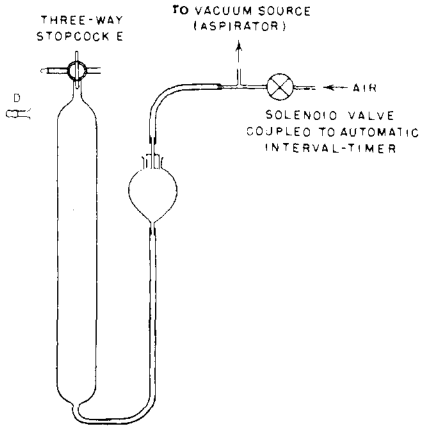

Fig. 2.—Gasometer and automatic mixer.

In one experiment, an aqueous solution of 0.0104 mole of methylethyl-*n*-propylamine oxide containing 0.031 mole of sodium hydroxide was concentrated to a thick sirup. The decomposition and the isolation of the products was carried out in the manner described above.

In order to obtain a homogeneous sample of the mixture of olefins for vapor-phase chromatographic analysis, the gaseous contents of the gasometer and olefin trap (while the two were still connected together) were thoroughly mixed by compressing and expanding them alternately and continuously for 6–12 hr. through the device diagrammed in Fig. 2. The automatic interval-timer opened and closed the solenoid valve at 10-sec. intervals. The vacuum created by an aspirator when the valve was closed caused the mercury in the levelling bulb to rise which in turn expanded the volume of the gases in the gasometer by more than 100 ml. Opening the solenoid valve released the vacuum and caused a compression of the gases.

After the gases were mixed, the gasometer was closed by stopcock E, and the olefin trap was replaced by a rubber serum cap D. The path between E and D was then evacuated before admitting the mixture of gases from the gasometer. Samples (0.2–0.4 ml.) for analysis were removed through D by means of a hypodermic syringe and injected into the chromatographic column in the manner described by Ray.[36]

The mixtures of olefins, with the exceptions of the isomeric butenes and *cis*- and *trans*-2-pentene, were separated by a 183 × 0.3-cm. column of 30% by weight carbethoxydimethylformamide impregnated on Celite 545 of 100–200 mesh size with helium as the eluent. The mixture of 1-butene and *cis*- and *trans*-2-butene was analyzed by a similar column packed with 30% by weight dimethylformamide on Celite 545 and cooled to −30°, while the mixture of *cis*- and *trans*-2-pentene was separated by saturated silver nitrate in diethylene glycol, both with helium as eluent. In all cases, a thermal conductivity cell was used as a detector.

The composition of each olefin mixture was computed from the chromatogram by determining the ratios of the individual peak areas. The individual peak areas were measured by the method of Cremer and Muller,[37] employing the product of peak height and half-band width, and were multiplied by a response factor which was obtained from the ratios of the areas produced by equal gaseous volumes of the standard olefins which comprised the mixture analyzed. The corrected area ratios gave directly the relative concentrations of the components in the mixture. Each ratio reported in Table VI and VII is the average of the ratios obtained from the analyses of two or more separate mixtures of olefins produced from decompositions of the same amine oxide or quaternary base. By the above procedure, each *ratio* was determined with an average deviation of 1–3% when the concentrations of the components in the mixture did not differ widely and of 6% when the mixture consisted mainly of one olefin. On the basis of numerous calibration experiments carried out during the course of this work, it is estimated that the absolute errors of the analyses are not significantly different from these deviations.

The volatile components of the olefin mixtures that were obtained from decomposition of the amine oxides and quaternary bases that produce either styrene or 1-decene were obtained by the procedure described above, whereas the other olefins (styrene or 1-decene) were isolated as liquids by the methods which follow. The mixture of water, dialkylhydroxylamine (or tertiary amine) and styrene retained in the first tube of the decomposition apparatus (Fig. 1) was kept at 0° and stirred with a magnetic stirrer throughout the elution process. The mixture was diluted with ethanol and the concentration of styrene was determined by comparison against standards with a Beckman DU spectrophotometer. The mixture of reaction products obtained from methyl-*n*-propyl-*n*-decylamine oxide and dimethyl-*n*-propyl-*n*-decylammonium hydroxide, after removal of the propylene, was extracted with three 20-ml. portions of purified pentane. The combined pentane extracts were washed with 10 ml. and 5 ml. portions of 2.5 *N* hydrochloric acid, then with 5 ml. of water and dried over anhydrous magnesium sulfate. The pentane was removed by distillation, and the residue, after weighing, was analyzed by vapor-phase chromatography to determine the concentration of 1-decene.

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[36] N. H. Ray, *J. Appl. Chem.*, **4**, 82 (1954).

[37] E. Cremer and R. Muller, *Z. Elektrochem.*, **55**, 217 (1951); M. Dimbat, P. E. Porter and F. H. Stross, *Anal. Chem.*, **28**, 290 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Amine Oxides. IV. Alicyclic Olefins from Amine Oxides and Quaternary Ammonium Hydroxides[1,2]

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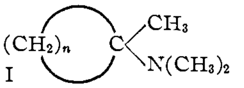
RECEIVED MARCH 11, 1957

Thermal decompositions of the N-oxides of N,N-dimethyl-1-methylcycloalkylamines containing five-, six- and seven-membered rings have been shown to give olefins containing 97.5, 2.8 and 84.8%, respectively, of the endocyclic isomers. The corresponding quaternary ammonium hydroxides follow the Hofmann rule when thermally decomposed to yield mainly the methylenecycloalkanes. These results are interpreted in terms of the steric requirements of these various ring systems. Pyrolyses of the amine oxides and quaternary hydroxides derived from N,N-dimethylcycloalkylmethylamines have been shown to produce exclusively the expected methylenecycloalkanes in all cases but one. Trimethylcyclopentylmethylammonium hydroxide gave appreciable amounts of 1-methylcyclopentene. Possible mechanisms for the formation of this product are discussed.

Earlier work comparing the selective formation of olefins from unsymmetrical amine oxides and quaternary ammonium hydroxides has shown that these thermal decompositions give results that are quite similar except in cases where steric interactions influence the direction of elimination of quaternary ammonium ions but not amine oxides.[2] Because of the steric interactions associated with alicyclic compounds, a study of the effect of ring size on the course of the two elimination reactions was undertaken. The olefins formed on thermal decomposition of amine oxides and quaternary ammonium hydroxides derived from homologous N,N-dimethyl-1-methylcycloalkylamines (I, *n* = 4, 5, 6) were examined, in order to determine the relative amounts of methylenecycloalkane (Hofmann rule elimination) and 1-methylcycloalkene (Saytzeff rule elimination). In addition, the thermal decompositions of the amine oxides and quaternary ammonium hydroxides of the N,N-dimethylcycloalkylmethylamines, II (*n* = 4, 5, 6), were investigated.


I


II

The compounds of type I were prepared by application of the Ritter reaction[4] to the olefins obtained by dehydration of the corresponding 1-methylcycloalkanols. Properties of the six tertiary amines that were employed in this study, I and II (*n* = 4, 5, 6), are summarized in Table I. The picrates, prepared as crystalline derivatives, are listed in Table II. The corresponding amine oxides were prepared by allowing the amines to react with aqueous hydrogen peroxide. The methiodides of the tertiary amines (Table III) were prepared and converted to the quaternary hydroxides.

Two thermal decompositions of each amine oxide and quaternary base were conducted. The olefins were analyzed by vapor-phase chromatography, and the relative amounts of exo- and endo-cyclic

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[1] Sponsored by the Office of Ordnance Research, U. S. Army, under Contract No. DA-19-020-ORD-3226, Project TB 2-0001(1112).

[2] Paper III, THIS JOURNAL, **79**, 4720 (1957).

[3] United States Rubber Co. Fellow, 1954–1955.

[4] J. J. Ritter and J. Kalish, THIS JOURNAL, **70**, 4048 (1948).