since the isocyanate groups are insulated from the electron-withdrawing benzene ring in the former type. It is surprising that the substituent effects are of the same order of magnitude for both the phenyl and benzyl types. Also, the benzyl type does have a higher energy of activation than the phenyl type. The extrapolation using the Arrhenius equation shows that the rates converge for the two classes at about 170°.

It is interesting to note that the isocyanate group *ortho* to the methyl group in *m*-tolylene diisocyanate is severely hindered in rate. However, the *meta t*-butyl group in 5-*t*-butyl-1,3-xylylene diisocyanate does not cause an appreciable change in the rate of reaction of either of its neighboring isocyanate groups compared to unsubstituted 1,3-xylylene diisocyanates.

Acknowledgment.—The authors wish to acknowledge the invaluable assistance of Dr. L. Tornheim and Mrs. C. L. Jensen in the mathematical and programming problems. This work was supported by the Oronite Chemical Co.

RICHMOND, CALIF.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

Carbanions. II. Cleavage of Tetraalkylammonium Halides by Sodium in Dioxane[1,2]

BY ERLING GROVENSTEIN, JR., ELWOOD P. BLANCHARD, JR., DAVID A. GORDON AND ROBERT W. STEVENSON

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Quaternary ammonium salts react with sodium in boiling dioxane to give alkane and tertiary amine by reductive cleavage and olefin and tertiary amine by an accompanying Hofmann-type elimination. Tetramethylammonium halides, in addition to methane and trimethylamine, give small amounts of ethylene and ethyldimethylamine. Ethylene is also a minor component of the olefins produced from other quaternary ammonium halides having at least one N-methyl group. Cleavage of salts of the type $R_n(CH_3)_{4-n}NX$ permits measurement of the relative amounts of RH and CH_4 produced. The ratio of RH to CH_4 obtained, after statistical correction for unequal numbers of groups and multiplication by 100, is: *n*-Pr, 2.4 ± 0.3; *n*-Bu, 2.6 ± 0.7; Et, 4.2 ± 0.5; *i*-Pr, 28.2 ± 1.9; *s*-Bu, 53 ± 3; Me, 100; allyl, 1050 ± 120; *t*-Bu, 10,800 ± 1000. Similar reductive cleavages of quaternary ammonium salts can be obtained in dioxane–*t*-amyl alcohol mixture and in cumene. Dioxane is not appreciably cleaved by sodium but is cleaved by sodium–potassium alloy to give ethylene and some ethylene glycol. Methyl *t*-butyl ether was not appreciably cleaved under any of the conditions tried with sodium and sodium–potassium alloy.

The reductive cleavage of quaternary ammonium salts to hydrocarbon and tertiary amine by reaction with an excess of sodium amalgam in aqueous or aqueous alcoholic medium is known as the Emde degradation. An example[3] is

$$C_6H_5CH{=}CHCH_2N(CH_3)_3Cl + 2Na + H_2O \longrightarrow$$
$$C_6H_5CH{=}CHCH_3 + N(CH_3)_3 + NaCl + NaOH$$

The ease of cleavage of groups as hydrocarbon component is $R\overset{\overset{O}{\|}}{C}CH_2$, $C_6H_5CH{=}CHCH_2 > C_6H_5CH_2 > CH_2{=}CHCH_2 > C_6H_5 \geq CH_3$ as judged by competitive cleavage of groups from quaternary ammonium cations containing two or more such groups.[4] Such an order of relative reactivity might be expected if either a carbanion or a free radical were produced as reactive intermediate in the product-determining stage of the reaction.

It occurred to us that for saturated alkyl groups carbanion and free radical stability are affected in different ways by alkyl substitution at the trivalent carbon atom and, therefore, that a study of the relative ease of cleavage of saturated alkyl groups might provide information concerning the nature of the Emde degradation. A practical difficulty to such a study, however, is the report of Emde and coworkers that ammonium compounds with four saturated alkyl groups are not cleaved by sodium amalgam. Thus Emde and Kull[4g] reported that N,N-dimethylpiperidinium chloride is not cleaved and similar results were obtained for methyldiethyl-β-hydroxyethylammonium chloride[5] and related compounds.[6] Methyl cleavage, however, has been observed in some cases. Thus v. Braun and Aust[4c] reported that 40% of the tertiary amine from reaction of N,N-dimethyltetrahydroquinolinium chloride with sodium amalgam was N-methyltetrahydroquinoline. Although methane would be expected as a corresponding product from this reaction, Emde and Kull[4g] have suggested, without citing evidence, that methyl alcohol is produced instead. Groenewoud and Robinson[4h] in their study of cleavage of aryltrimethylammonium chloride by sodium amalgam obtained 5 to 80% of aryldimethylamine, depending upon the aryl group. These authors did not identify the fate of the methyl group in their cleavages; however they did show that their quaternary ammonium chlorides were unreactive toward sodium hydroxide under conditions which were rather similar to those employed in their reactions with sodium amalgam. It accordingly seems probable, as they suggested, that the methyl group appeared as

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(1) More extensive experimental details are recorded in theses at the Georgia Institute of Technology: D. A. Gordon, Ph.D. thesis, June, 1953; E. P. Blanchard, Jr., M.S. thesis, June, 1954; R. W. Stevenson, Ph.D. thesis, May, 1958.

(2) Paper I in this series is considered to be that of E. Grovenstein, Jr., THIS JOURNAL, **79**, 4985 (1957).

(3) H. Emde, *Arch. Pharm.*, **244**, 289 (1906).

(4) (a) H. Emde, *ibid.*, **247**, 369 (1909); **249**, 106 (1911); (b) H. Emde and P. Schellbach, *ibid.*, **249**, 118 (1911); (c) J. v. Braun and E. Aust, *Ber.*, **49**, 501 (1916); (d) J. v. Braun and L. Neumann, *ibid.*, **50**, 50 (1917); (e) J. v. Braun, J. Seemann and A. Schultheiss, *ibid.*, **55**, 3803 (1922); (f) T. S. Stevens, E. M. Creighton, A. B. Gordon and M. MacNicol, *J. Chem. Soc.*, 3193 (1928); (g) H. Emde and H. Kull, *Arch. Pharm.*, **272**, 469 (1934); (h) P. Groenewoud and R. Robinson, *J. Chem. Soc.*, 1692 (1934).

(5) H. Emde and A. Runne, *Arch. Pharm.*, **249**, 371 (1911).

(6) H. Emde, *Helv. Chim. Acta*, **15**, 1330 (1932).

TABLE I

PRODUCTS FROM SIMPLE TETRAALKYLAMMONIUM HALIDES WITH SODIUM IN DIOXANE

Salt reacted	Reaction time, min.	Yield,[a] % Alkane	Alkene	Amines (total)
$(CH_3)_4NCl$	1020[b]	50.3 methane[d]	6.9 ethylene	65.5
$(CH_3)_4NCl$	87[c]	72.7 methane[d]	1 ± 1	80.2
$(CH_3)_4NBr$	420	47.4 methane	3.1 ± 0.6 ethylene[e]	48.7[f]
$(C_2H_5)_4NBr$	~90	35.0 ± 1.2 ethane	52.0 ± 1.2 ethylene[g]	80
$(n\text{-}C_4H_9)_4NBr$	3	46.2 *n*-butane	33.9 butene-1[e]	..

[a] All yields are calculated as 100 times the ratio of moles of product to moles of ammonium salt taken for reaction. [b] Isopropyl alcohol (0.0026 mole) was added in increments in an attempt to accelerate this reaction. [c] Run in a solvent consisting of 110 ml. of dioxane and 140 ml. of *t*-amyl alcohol. [d] The yield is by Orsat combustion to carbon dioxide and is based on the assumption that the saturated hydrocarbon consisted entirely of methane. [e] Infrared absorption indicated the presence of a trace of acetylene. [f] The yields of individual amine were 48.1% trimethylamine, 0.6 ± 0.2% ethyldimethylamine. [g] No butene-1 detectable by infrared absorption.

TABLE II

PRODUCTS FROM QUATERNARY AMMONIUM HALIDES, $R_n(CH_3)_{4-n}NX$, WITH SODIUM IN DIOXANE

Salt reacted $R_n(Me)_{4-n}NX$	Reaction time, min.	Yield,[a] % Volatile amine	Total alkene	CH_4	RH	Observed ratio 100(RH/CH_4)	Corrected ratio $100\left(\frac{4-n}{n}\right)$(RH/$CH_4$)
n-Bu_3MeNI	3–18	..	22.0 ± 0.7	55.5 ± 1.4	3.13 ± 0.08	5.64 ± 0.16	1.88 ± 0.05
n-Bu_3MeNBr	8	..	35.0 ± .8	45.3 ± 1.9	2.91 ± .04	6.4 ± .4	2.14 ± .12
n-Bu_3MeNBr	10	..	37.0 ± .8	51.8 ± 1.6	3.36 ± .04	6.5 ± .3	2.16 ± .09
n-$BuMe_3NI$	11	23.6	21.5 ± 1.1	67.0 ± 1.9	0.70 ± .03	1.04 ± .07	3.1 ± .2
n-$BuMe_3NI$	14	21.4	17.3 ± 1.0	73.7 ± 1.5	0.69 ± .03	0.94 ± .05	2.82 ± .15
n-$BuMe_3NCl$	80	28.1	25.3 ± 1.4	33.8 ± 0.7	0.36 ± .03	1.06 ± .11	3.2 ± .3
n-$BuMe_3NCl$	62	25.6	23.8 ± 1.3	33.3 ± 0.8	0.31 ± .03	0.93 ± .12	2.8 ± .4
s-$BuMe_3NI$	54	30.9	13.7	64.2 ± 3.2	10.8 ± .3	16.8 ± 1.4	50 ± 4
s-$BuMe_3NI$	15	37.1	19.2 ± 1.0	66.5 ± 1.5	12.1 ± .2	18.2 ± 0.7	55 ± 2
t-$BuMe_3NI$	173	..	5.3 ± 0.7	1.36 ± 0.08	50.1 ± 1.4	3700 ± 300	11,100 ± 900
t-$BuMe_3NI$	100	48.8	5.5 ± 0.8	1.20 ± 0.12	41.9 ± 1.0	3500 ± 400	10,500 + 1200
Et_3MeNI	15	8.4	9.1 ± 1.3	84.0 ± 1.8	9.97 ± 0.09	11.9 ± 0.4	3.96 ± 0.12
Et_3MeNI	12	..	8.3 ± 1.5	88.0 ± 3.4	10.1 ± .14	11.5 ± .7	3.8 ± .2
Et_3MeNCl	24	73.2[b]	57.4 ± 1.9	26.2 ± 0.5	3.66 ± .06	14.0 ± .6	4.7 ± .2
Et_3MeNCl	17	71.8[b]	49.5 ± 1.8	23.4 ± 0.5	3.40 ± .07	14.5 ± .6	4.8 ± .2
$EtMe_3NBr$	63	61.4	34.8 ± 1.4	57.5 ± 2.5	0.80 ± .06	1.39 ± .15	4.2 ± .5
$EtMe_3NBr$	99	62.2	39.6 ± 1.6	52.3 ± 1.5	0.65 ± .07	1.24 ± .15	3.7 ± .5
n-$PrMe_3NI$	14	32.5	28.0 ± 0.7	57.3 ± 1.3	0.43 ± .04	0.75 ± .09	2.3 ± .3
n-$PrMe_3NI$	10	31.8	27.4 ± 1.5	55.9 ± 1.9	0.47 ± .05	0.84 ± .12	2.5 ± .4
i-$PrMe_3NI$	13	21.0	9.2 ± 0.9	80.2 ± 2.0	7.8 ± .2	9.7 ± .6	29.1 ± 1.8
i-$PrMe_3NI$	17	27.6	6.5 ± 0.8	51.7 ± 1.6	4.9 ± .2	9.5 ± .7	28.4 ± 2.0
Allyl Me_3NCl	480	29.6	22.3 ± 0.6	6.4 ± 0.6[c]	....	350 ± 40[d]	1050 ± 120[d]

[a] All yields are calculated as 100 times the ratio of moles of product to moles of ammonium salt taken for reaction. [b] The yield of amine includes both the volatile amine and that which codistilled with the solvent. [c] The yield is *via* Orsat combustion. [d] This is calculated as the ratio of alkene (propylene) to methane.

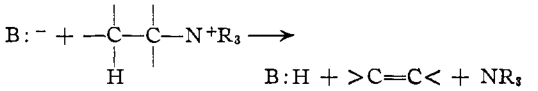
methane rather than as methanol in these cleavages.

The most probable explanation of why sodium amalgam cleaves saturated alkyl groups with difficulty, if at all, from saturated tetraalkylammonium salts is that there is a competing faster reaction of the sodium with the aqueous or alcoholic solvent to liberate hydrogen instead of alkane.[7] We have accordingly studied the reductive cleavage of tetraalkylammonium salts in less reactive solvents than water or ethanol. Dioxane, dioxane–*t*-amyl alcohol mixture, and cumene were employed as media in the present work.

Discussion of Results

The products which result upon reaction of molten sodium in dioxane with quaternary ammonium halides having only one type of alkyl group attached to nitrogen are summarized in Table I while in Table II reactions of quaternary salts having two types of alkyl groups (one always being methyl) are presented. Under these conditions two major types of reaction occur—one is reductive cleavage leading to saturated hydrocarbon and tertiary amine and the other is elimination giving olefin and tertiary amine. The ratio of olefin formation to reductive cleavage is of only moderate reproducibility for any one salt as shown by the tables. Moreover, this ratio is highly dependent upon the halide anion present; thus while triethylmethylammonium chloride gave about the highest ratio of olefin to alkane, triethylmethylammonium iodide gave nearly the lowest ratio.

Olefin formation appears to result from Hofmann-type elimination



$$B:^- + -\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{|}{C}}-N^+R_3 \longrightarrow B:H + {>}C{=}C{<} + NR_3 \quad (1)$$

where B:⁻ is a carbanion or an alkoxide anion derived from the solvent. That alkoxide anions can promote such eliminations under conditions

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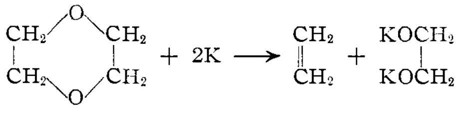
[7] We were initially lead to this conclusion upon discovering methane as one of the prominent products from reaction of ω-chloroalkyltrimethylammonium chlorides with sodium in dioxane (unpublished research).

similar to those used for the reaction was demonstrated by the reaction of sodium *t*-amyloxide with tetra-*n*-butylammonium bromide to give a good yield of butane-1 in a refluxing solvent consisting of a mixture of dioxane and *t*-amyl alcohol. The alkoxide anion which is derived from dioxane is presumably $CH_2{=}CHOCH_2CH_2ONa$, as postulated below. Reaction 1 converts the alkoxide into the corresponding alcohol which in turn may react with sodium to regenerate the alkoxide. Thus the concentration of alkoxide required to promote reaction 1 is not necessarily high.

Table I shows, rather surprisingly, that ethylene is a product of reaction of tetramethylammonium salts with sodium in dioxane. Moreover ethylene was produced in 1 to 2% yield from corresponding reactions of *n*-butyltrimethylammonium iodide, *s*-butyltrimethylammonium iodide and *t*-butyltrimethylammonium iodide. Probably ethylene was a minor component of all the olefins obtained from quaternary ammonium salts having at least one N-methyl group. One possible source of ethylene would be from the dioxane used as solvent. While previous workers[8] do not appear to have noted any reaction between refluxing dioxane and sodium–potassium alloy, in the present work dioxane was found to undergo slow cleavage to ethylene upon vigorous stirring with this alloy after addition of a little oleic acid as dispersing agent. The reaction is evidently



although ethylene glycol actually was isolated in only low yield relative to the ethylene produced. With sodium alone, however, no appreciable amount of ethylene was obtained from dioxane under any of the conditions investigated in the present work. We conclude, therefore, that most of the ethylene produced during the reaction of tetramethylammonium and other N-methylammonium halides with sodium came from a reaction involving the salts themselves and not from cleavage of the dioxane.

A clue to the source of ethylene from tetramethylammonium halides and sodium is provided by evidence (see Experimental Details) for the presence of ethyldimethylamine in the amines formed during the reaction. This reaction path leading to ethylene is suggested

$$(CH_3)_4N^+ + 2Na \longrightarrow CH_3{:}^-Na^+ + (CH_3)_3N \quad (2)$$

$$(CH_3)_4N^+ + CH_3{:}^-Na^+ \longrightarrow {:}^-CH_2N^+(CH_3)_3 + CH_4 + Na^+ \quad (3)$$

$${:}^-CH_2N^+(CH_3)_3 + (CH_3)_4N^+ \longrightarrow CH_3CH_2N^+(CH_3)_3 + (CH_3)_3N \quad (4)$$

$$CH_3CH_2N^+(CH_3)_3 + B{:}^- \longrightarrow CH_2{=}CH_2 + BH + N(CH_3)_3 \quad (5)$$

The reasons for writing reaction 2 will be presented later. Reaction 3 is analogous to the reaction of phenyllithium with tetramethylammonium ion to give an "ylide" as discovered by Wittig[9] and co-workers. Reaction 4 is analogous to the second step of the Wurtz reaction[10] but with an ammonium cation rather than an alkyl halide as alkylating agent. Reaction 5 is a special case of the general reaction 1 discussed above. That ethyltrimethylammonium cation can react qualitatively in the way postulated is confirmed by the data for ethyltrimethylammonium bromide shown in Table II. These data suggest that more ethyldimethylamine should have been isolated than was found in the reaction with tetramethylammonium bromide. The difference is perhaps to be accounted for on the basis of the different environment in which ethyltrimethylammonium bromide existed in the two heterogeneous reactions.

When tetramethylammonium chloride was treated with sodium in a solvent consisting of 110 ml. of dioxane with 140 ml. of *t*-amyl alcohol, little, if any, olefin was formed and that which may have been formed probably was not ethylene (see below). This result is explained readily in terms of the reaction sequence presented above: namely, that *t*-amyl alcohol should destroy methylsodium as rapidly as it is produced by the reaction

$$CH_3{:}^-Na^+ + C_5H_{11}OH \longrightarrow CH_4 + C_5H_{11}O^-Na^+$$

Reaction 3 and in turn 4 and 5 would therefore be blocked. In the early stages of the present work we proposed to use *t*-amyl alcohol to block side reactions of this type. As our work developed, however, it eventually became evident, after many misleading results, that our *t*-amyl alcohol underwent a reaction with sodium which gave saturated and unsaturated hydrocarbons in the ratio of about six to one. Evidently these came from some impurity(s) in the *t*-amyl alcohol used (see Experimental Details). The use of *t*-amyl alcohol, therefore, had to be abandoned because the hydrocarbons produced from it interfered with our analysis, by infrared absorption, for the hydrocarbons from quaternary ammonium salts. The cleavage of tetramethylammonium chloride went much faster in dioxane–*t*-amyl alcohol than in dioxane alone presumably because of the greater solubility of the ammonium salt in the alcoholic solvent.

With tetraethylammonium bromide, no side reaction analogous to that discussed above for tetramethylammonium bromide was evident. In particular no butene-1 was detected in the olefin from tetraethylammonium bromide. Evidently the analogs of reactions 3 and 4 occur slowly, if at all, when higher alkyl groups than methyl are involved.

In the reaction of tetramethylammonium bromide with sodium in dioxane, no ethane was detected in the infrared spectrum of the saturated hydrocarbon (methane) from the reaction. Indeed if the ratio of ethane to ethylene in this reaction were to exactly parallel that from ethyltrimethylammonium bromide, only about 0.05% of ethane would have been expected; such a small amount of ethane could have escaped detection. The important point of this discussion is that while the side reaction leading to a little ethylene contributes somewhat to the over-all yield of olefin, such side reaction should not complicate appreciably the

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[8] J. B. Conant and A. H. Blatt, THIS JOURNAL, **50**, 551 (1928).

[9] G. Wittig and W. Merkle, *Ber.*, **76**, 109 (1943); G. Wittig and Wetterling, *Ann.*, **557**, 193 (1947).

[10] A. A. Morton, J. B. Davidson and B. L. Hakan, THIS JOURNAL, **64**, 2242 (1942).

saturated hydrocarbons produced from the reaction.

The second column from the right of Table II presents the ratio of alkane to methane multiplied by one hundred. For the butylmethylammonium halides this ratio varies by a factor of seven from the lowest to the highest value. In the column at the far right of this table, this ratio is corrected for unequal numbers of *n*-butyl and methyl groups present in the quaternary ammonium salt by multiplication by the statistical factor $(4 - n)/n$, where n is the number of butyl (or higher alkyl) groups attached to a single nitrogen atom. The corrected ratio for the butylmethylammonium halides now varies only 1.7-fold from the lowest to the highest value or the average value is 2.6 with a maximum deviation of ±0.7 or an average deviation of ±0.5. For the ethylmethylammonium halides while the observed ratio varies from lowest to highest value by a factor of 11.7-fold the statistically corrected ratio is nearly constant at an average value of 4.2 with a maximum deviation of ±0.6 or an average deviation of ±0.4. While in a number of cases the deviations of the individual values from the average exceed the expected experimental errors in the determination of the corrected ratios, the maximum deviation for the *n*-butyl compounds was only some 3.5 times the expected average experimental error and for the ethyl compounds only two times the expected average experimental error. The near constancy of these corrected ratios, regardless of the number of alkyl groups present or the nature of the halide ion and despite the variableness in the yield of olefin and of the heterogeneous nature of the reaction, suggests that this ratio is a measure of some fundamental property of alkyl groups attached to quaternary nitrogen.

Averaging the corrected ratios for each type of group and arranging the groups according to increasing rate of cleavage relative to methyl, which for convenience is assigned a rate of 100, gives the sequence: *n*-Pr, 2.4 ± 0.3; *n*-Bu, 2.6 ± 0.7 < Et, 4.2 ± 0.5 < *i*-Pr, 28.2 ± 1.9 < *s*-Bu, 53 ± 3 < Me, 100 < allyl, 1050 ± 120 < *t*-Bu, 10,800 ± 1000. The relative rate of cleavage of alkyl groups from nitrogen does not vary in a simple manner with structure. Thus replacement of the hydrogen atoms of the methyl group with methyl groups first causes a large decrease in rate, then a moderate increase in rate and finally a very large increase in rate on passing from methyl to ethyl to isopropyl to *t*-butyl. On the other hand, the three primary alkyl groups above methyl react at about the same rate within a factor of two as do also the two secondary alkyl groups which were tested. For interpretation of the influence of structure upon ease of cleavage of alkyl groups some knowledge of mechanism appears essential.

Emde[11,4g] has suggested that first the quaternary ammonium salt dissociates into alkyl halide and tertiary amine and subsequently the alkyl halide is reduced by sodium and water to hydrocarbon. Thus for benzyltrimethylammonium chloride Emde's scheme is

$$C_6H_5CH_2N^+(CH_3)_3 + Cl^- \longrightarrow C_6H_5CH_2Cl + N(CH_3)_3$$

$$C_6H_6CH_2Cl + 2Na(Hg) + H_2O \longrightarrow C_6H_5CH_3 + NaCl + NaOH$$

While undoubtedly alkyl halides can be reduced under the reaction conditions to hydrocarbons, the prior dissociation of a quaternary ammonium halide into alkyl halide and amine should not in general occur at a fast enough rate to account for appreciable reaction. This conclusion is supported by Collie and Schryver's[12] observation that the approximate temperature for decomposition of quaternary ammonium salts (thus for $C_6H_5N(CH_3)_3Cl$, $C_6H_5CH_2N(CH_3)_3Cl$ and $CH_3CH_2N(CH_3)_3Cl$) is somewhat above 300°. Extrapolation of these results to the temperature of refluxing dioxane suggests that the rate of decomposition of quaternary ammonium salts at 101° is too small to account for the rate of reductive cleavage. In the present work no decomposition of tri-*n*-butylmethylammonium iodide in refluxing dioxane-*t*-amyl alcohol could be detected over a period of one hour while the reductive cleavage of this salt was completed in three to eighteen minutes in dioxane (depending upon the rate of stirring), or somewhat more readily in dioxane-*t*-amyl alcohol.

It might be argued that for the reaction

$$ArN^+(CH_3)_3 + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ArN(CH_3)_2 + CH_3Cl,$$

the forward reaction (k_1) occurs readily at 100° but is not apparent because the reverse reaction (k_{-1}) occurs even more readily; indeed at such temperature k_{-1} must be considerably greater than k_1 because the reaction to give quaternary ammonium salt has a favorable equilibrium constant. On the other hand, the reaction

$$ArN^+(CH_3)_3 + OH^- \xrightarrow{k_2} ArN(CH_3)_2 + CH_3OH$$

is not appreciably reversible in an alkaline medium at 100°. Now Groenewoud and Robinson[4h] reported that quaternary ammonium salts of the type $ArN^+(CH_3)_3Cl^-$ were stable toward 8% sodium hydroxide at 100° for eight hours (no reaction). Now since hydroxide anion is in general more nucleophilic[13] than chloride anion k_1 must be smaller than k_2 at 100°. Therefore since k_2 is inappreciable, k_1 must be inappreciable also compared to the rate of reductive cleavage. While these arguments have been developed for quaternary chlorides, the bromides and iodides of Table II gave alkane to methane ratios which were so similar to those for the corresponding chlorides that surely the mechanism of reductive cleavage of chlorides, bromides and iodides must be similar. We therefore conclude that Emde's mechanism cannot be applicable to the present ammonium salts under the conditions investigated.

The reaction path (6)-(7) is proposed for the reductive cleavage of quaternary ammonium salts

$$R_4N^+ + 2Na \longrightarrow R\!:^- + R_3N + 2Na^+ \qquad (6)$$

$$R\!:^- + A\!:\!H \longrightarrow RH + A\!:^- \qquad (7)$$

We leave open for discussion in an accompanying

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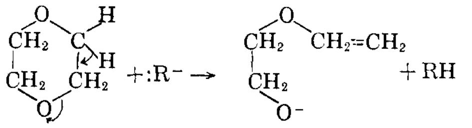
(11) H. Emde, *Arch. Pharm.*, **247**, 314 (1909).

(12) N. Collie and S. B. Schryver, *J. Chem. Soc.*, **57**, 767 (1890).

(13) C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

paper[14] the question of whether the reaction represented by equation 6 occurs by two one electron transfers or, in a single step, by a two electron transfer process. Furthermore, reaction 6 evidently occurs at the surface of a particle of sodium metal and possibly the carbanion formed should be represented as being absorbed on the particle of sodium. In equation 7, AH represents a proton donor. One possible proton donor is an unreacted molecule of quaternary ammonium salt (see equation 1); this reaction path leads to olefin. Since olefin frequently was formed in low yield (see Table II) quaternary ammonium ions cannot be the only or frequently the major source of hydrogen for reductive cleavage. Evidently the dioxane used as solvent is the major source of hydrogen. The following reaction is suggested



(8)

A small amount of acetylene (less than 1% yield based on the moles of ammonium salt reacted) was detected in the gaseous products from the reaction of the present ammonium salts in dioxane. Since acetylene was observed even with tetra-*n*-butylammonium iodide, it evidently did not originate from the ammonium salt but from the solvent. The reaction (9) seems reasonable

$$^{-}OCH_2CH_2OCH{=}CH_2 + R\!:^{-} \longrightarrow {}^{-}OCH_2CH_2O^{-} + RC{\equiv}CH + RH \quad (9)$$

Reactions 8 and 9 are analogous to the known cleavages of ethers by organoalkali reagents.[15]

Allyl ether is cleaved by potassium sand in *n*-decane at 30° to give allylpotassium[15b] and by sodium sand in hexane at 35° to give allylsodium.[16] Similarly allyl alcohols are known to undergo reductive cleavage with alkali metals to give propylene or derivative.[17] Now since the *t*-butyl group cleaved from quaternary nitrogen ten times faster than the allyl group as judged by competitive cleavages measured relative to methyl (Table II), it might be anticipated that *t*-butyl methyl ether would be cleaved by alkali metals. *t*-Butyl methyl ether, however, was not cleaved appreciably by sodium or potassium under any of the conditions tried in the present work.

The rates of cleavage of quaternary ammonium salts by sodium in dioxane are indicated approximately by the reaction times shown in Tables I and II. These reaction times were determined at approximately the same stirring rate save for the very reactive salts which required a lower rate in order to control the reaction. For the *n*-butylmethylammonium halides the larger the number of butyl groups present the faster the over-all rate of the reaction in spite of the fact that *n*-butyl groups cleave at about two-hundredths the relative rate of methyl groups (see the corrected ratios of Table II). The replacement of methyl groups by *n*-butyl groups increases the solubility of the ammonium salt. The reaction times of the tables are approximately inversely proportional to the expected solubility of the salts. Conceivably also the more soluble salts are better surface-active agents and give rise to sodium dispersions of smaller particle size.

Because of these and other known complications of heterogeneous reactions a more detailed consideration of the results of the present work will be deferred until after data are presented for the more nearly homogeneous cleavages in liquid ammonia in Part III.[14]

Experimental Details[18]

Reagents.—Except as noted below, the amines and alkyl halides which were used in the preparation of quaternary ammonium salts were of the best available commercial grades and, except for the methylamines and methyl halides, were subjected to fractional distillation before use. *n*-Butyldimethylamine, b.p. 93° at 738 mm. (recorded[19] b.p. 95°), was obtained from reaction of *n*-butyl bromide with dimethylamine.

The following amines were obtained in the yields given by methylation of the recorded amine with formic acid and formaldehyde according to the procedure of Icke and Wisegarver[20] except that the methylation mixture was kept at 85 to 95° for the time recorded: di-*n*-butylmethylamine,[21] b.p. 161.2–162.2° at 749 mm., in 84% yield from di-*n*-butylamine with heating of the methylation mixture 24 hours; *sec*-butyldimethylamine,[22] b.p. 92.8–93.0° at 739 mm., in 64% yield from *sec*-butylamine with heating for 39 hours; *t*-butyldimethylamine,[23] b.p. 88.3–89.2° at 740 mm., in 85% yield from *t*-butylamine with heating for 24 hours; isopropyldimethylamine,[24] b.p. 63.8–64.2° at 740 mm., in 41% yield (some accidental losses) from isopropylamine with heating for 60 hours.

The hydrocarbons used for calibration of infrared analyses, *n*-butane, isobutane and propane, were obtained from Matheson Co., Inc., while methane and ethane were from Phillips Petroleum Co. The minimum purity of all of these hydrocarbons was at least 99.5%. Butene-1 and isobutylene were from Matheson Co. and were of 99.0% minimum purity.

t-Amyl alcohol, from Matheson, Coleman and Bell, was refluxed over sodium for 6 hours and then distilled from sodium at b.p. 101.0–102.0° at 738 mm.

Cumene was purified by the method of Vogel,[25] but was refluxed over sodium for two hours with stirring by a Morton high-speed stirrer, and distilled under nitrogen at 151.9–152.8° at 739 mm.

1,4-Dioxane was purified by the method of Hess and Frahn.[26] Tetrahydrofuran was refluxed with potassium with high-speed stirring for one hour and then distilled. *t*-Butyl methyl ether was from Eastman Kodak Co. and distilled at 52–53.5° at 745 mm.

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[14] E Grovenstein, Jr., and R. W. Stevenson, This Journal, **81**, 4850 (1959).

[15] (a) A. A. Morton, *Chem. Revs.*, **35**, 21 (1944); (b) A. A. Morton, E. E. Magat and R. L. Letsinger, This Journal, **69**, 950 (1947); (c) R. L. Letsinger, A. W. Schnizer and E. Bobko, *ibid.*, **73**, 5708 (1951); (d) R. L. Letsinger and E. Bobko, *ibid.*, **75**, 2649 (1953).

[16] R. J. Letsinger and J. G. Traynham, *ibid.*, **70**, 3342 (1948).

[17] A. J. Birch, *Quart. Rev.* (*London*), **4**, 69 (1950).

[18] All melting points are corrected unless otherwise specified.

[19] H. T. Clarke, *J. Chem. Soc.*, **103**, 1696 (1913).

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

[21] Previously reported in 69% yield from *n*-butyl chloride and methylamine; O. Westphal and D. Jerchel, *Ber.*, **73**, 1002 (1940).

[22] Previously reported in 25% yield by hydrogenation of a mixture of methyl ethyl ketone and dimethylamine; A. C. Cope, N. A. LeBel, H. Lee and W. R. Moore, This Journal, **79**, 4720 (1957).

[23] Previously reported in low yield by methylation of *t*-butylamine with methyl iodide; N. Bortnick, L. S. Luskin, M. D. Hurwitz, W. E. Craig, L. J. Exner and J. Mirza, *ibid.*, **78**, 4040 (1956).

[24] Previously reported product of b.p. 67–67.5°, in some 17% yield as the hydrochloride, from hydrogenation of a mixture of acetone and dimethylamine; A. Skita and F. Keil, *Monatsh.*, **53/54**, 762 (1929).

[25] A. I. Vogel, *J. Chem. Soc.*, 607 (1948).

[26] L. F. Fieser, "Experiments in Organic Chemistry," third edition, D. C. Heath and Co., Boston, Mass., 1955, p. 285.

TABLE III

QUATERNARY AMMONIUM HALIDES PREPARED

Ammonium halide	Procedure[f]	Yield, %	M.p., °C.	Halogen, % Calcd.	Halogen, % Found
Allyl NMe_3Cl[a]	$RCl + NMe_3$ in MeOH 3 d. at 0°, 2 d. at 25°	92	Pic. 216–218[b]	26.14	25.97
$EtNMe_3Br$	$EtBr + NMe_3$ in MeOH 2 d. at −78°, slowly up to 25°	75	322–325.6 d.[e]	47.58	47.43
Et_3NMeCl[j]	$MeCl + Et_3N$ in MEK 4 d. at −78°, 3 d. near 20°[h]	97	284 d., uncor.	23.38	23.40
Et_3NMeBr[j]	$MeBr + Et_3N$ in DMK 1 hr. at −78°, slowly up to 25°	93	307.4 d.	40.74	40.51
Et_3NMeI[k]	$MeI + Et_3N$ in MeOH 15 hr. at −78°, 6 d. at 25°	100[i]	308.4–309.5 d.	52.19	52.00
t-$BuNMe_3I$	MeI + *t*-$BuNMe_2$ in MeOH 24 hr. at 0°,[c] 5 d. at 25°	99	260–260.5 d.[d]	52.19	52.32
n-$BuNMe_3Cl$	*n*-BuCl + Me_3N in MeOH 70 d. at 25°	74	223.7–224.0	23.40	23.28
n-Bu_2NMe_2Cl	*n*-BuCl + *n*-$BuNMe_2$ in MEK 10 d. at reflux	74	148–149	18.33	18.29
n-Bu_2NMe_2Br	MeBr + *n*-Bu_2NMe in DMK 1 hr. at −78°, slowly up to 25°	95	166.0–166.2	33.55	33.33
n-Bu_3NMeBr	MeBr + *n*-Bu_3N in DMK 4 hr. at 0°, 15 hr. at 25°	96	120.5–121.5	28.51	28.44
i-$PrNMe_3Br$	MeBr + *i*-$PrNMe_2$ in DMK 1 hr. at −78°, slowly up to 25°	91	317 d.	43.88	43.57
i-$PrNMe_3I$	MeI + *i*-$PrNMe_2$ in MEK 2 d. at −78°, slowly up to 25°	95	316–316.8 d.[g]	55.40	55.16

[a] *Cf.* E. Rothstein, *J. Chem. Soc.*, 1559, 1561 (1940); D. R. Howton, THIS JOURNAL, **69**, 2555 (1947). [b] The m.p. reported is that of the corresponding picrate. [c] Initial cooling in Dry Ice–acetone-bath. [d] See ref. 23. [e] M. J. McDowell and C. A. Kraus, *ibid.*, **73**, 2170 (1951), report 338°. [f] MEK, methyl ethyl ketone; DMK, acetone; d., day. [g] T. Kato, T. Morikawa and Y. Suzuki, *J. Pharm. Soc., Japan*, **72**, 1177 (1952); *C. A.*, **47**, 7433 (1953), report 286°. [h] Near room temperature under reflux afforded by Dry Ice cooled condenser. [i] Yield obtained by titration; the other yields are those of the isolated product. [j] *Cf.* L. Wagner, *Z. Kryst. Mineral.*, **43**, 186 (1906–1907). [k] *Cf.* W. J. Pope and J. Read, *J. Chem. Soc.*, 101, 528 (1912).

Quaternary Ammonium Halides.—All the quaternary ammonium salts used in the present work were heated at 50 to 85° in a vacuum oven overnight or longer as required to remove water or solvent. The salts were routinely analyzed for halogen by titrimetric procedures,[27] either with use of an absorption indicator or, where the absorption indicator failed to give a sharp end-point, by Volhard's method. Satisfactory halide analyses (within 0.3% of theory) were obtained in all cases save that of tri-*n*-propylmethylammonium iodide which failed to give a clear end-point in either titration. Tetraethylammonium bromide was Eastman Kodak Co. white label grade and demanded no further purification after drying.

Preparations of quaternary ammonium salts were made in tightly stoppered flasks with approximately equimolar amounts of amine and alkyl halide in one to three volumes of solvent per volume of reactants. After completion of the reaction, crystallization was enhanced by addition of anhydrous ethyl ether. In some cases, especially when methanol was the solvent, the solvent was largely removed prior to addition of ether by distillation under a stream of dry nitrogen. To complete crystallization the flasks were stored for several days in the cold (*ca.* 5°); when the product was oily, the solvent was removed by decantation and replaced by fresh anhydrous ether and the reaction mixture stored for several more days in the cold. The products were separated by suction filtration and washed with anhydrous ether; during these operations the filter flask was protected from water vapor from the water-pump by a calcium chloride drying tube and a rubber dam was placed over the top of the filter funnel. Frequently the ammonium compounds so obtained after drying *in vacuo* were sufficiently pure as indicated by halide analysis to require no further crystallization. In other cases the ammonium salts were recrystallized from *t*-butyl alcohol, isopropyl alcohol or a mixture of ethyl acetate and methanol. In Table III are summarized the preparations of new quaternary ammonium halides or halides whose properties and preparations are not adequately described elsewhere. Other quaternary ammonium halides used in this research were prepared in similar manner from tertiary amines and alkyl halides.

Reaction of Ammonium Halides with Sodium in Dioxane.—The apparatus consisted of a 500-ml. Morton flask (three necks, two creases, inverted cone) and a Morton high-speed stirrer.[28] To one of the side necks of the Morton flask was attached a vertical Vigreux column, some twenty inches long, which served to separate the volatile reaction products from the solvent, the condensed solvent being returned to the reaction flask. The gas outlet on the bearing housing of the Morton stirrer also was attached to the bottom of the Vigreux column and served as a valuable additional exit for gases from fast reactions. To the top of the column, a Claisen still-head was attached and led to a 500-ml. distillation receiver. To a side arm leading from the distillation receiver was attached a 250-ml. flask which acted as a safety trap. From the latter butyl rubber tubing led exit gases through two 500-ml. scrubbers containing coarse fritted glass bubblers. The scrubbers contained a known amount of 0.2 to 0.4 *M* hydrochloric acid and were used to remove volatile amines produced in the reactions. A tube led from the last scrubber to a 10- or 20-liter inverted gas collection bottle which was calibrated so as to enable the volume of gas collected to be estimated. Gas was collected by displacement of saturated brine from the gas collection bottle. A glass tube extending nearly to the top of the bottle permitted withdrawal of samples of gas for analysis. The reaction assembly was also attached to two mercury bubblers which served as valves; one allowed nitrogen to enter the system in case the pressure fell appreciably below atmospheric pressure and the other allowed gases to escape from the system if the pressure became excessively high. Provision also was made such that the system could be swept with nitrogen as desired.

All connections were held tight with wire and rubber bands or springs. The average yield of hydrocarbons recorded in the runs of Table II was 86% omitting the runs with *t*-butyltrimethylammonium iodide and allyltrimethylammonium chloride. It seems probable that the yield of hydrocarbons was actually nearly quantitative and that the lower yield found represents losses due to leakage of gas about the stirrer shaft. By means of moistened *p*H paper in several runs amine was detected leaking about the shaft. The tendency to leak seemed to increase with continued running of the stirrer; quantitative or nearly quantitative yields were often obtained when the reactions were fast. The slowest reactions—that of *t*-butyltrimethylammonium iodide, allyltrimethylammonium chloride and tetramethylammonium chloride and bromide (see Table I)—gave the lowest yield of hydrocarbon; losses from leakage doubtless account for the low yield in part, but possibly the slow reactions were not given adequate time for completion. It seems unlikely that loss of products by leakage seriously affected the ratio of methane to other hydrocarbon component in the product. This conclusion is supported by the data of Table II. Thus with isopropyltrimethylammonium iodide the pield of hydrocarbons in the two runs recorded was 97.2 and 63.1% while the ratio of methane to propane was constant within experimental error. Similarly a run on tri-*n*-butylmethylammonium bromide which gave 83.2% of hydrocarbons gave essentially the same ratio of methane to butane as another run which gave 92.2% of hydrocarbons. Moreover the runs on *n*-butyltrimethylammonium iodide which gave hydrocarbons in 89 to 92% yield gave, within experimental error, the same ratio of methane to butane as runs on *n*-butyltrimethylammonium chloride which gave

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(27) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," third edition, The Macmillan Co., New York, N. Y., 1952, pp. 543–546.

(28) A. A. Morton and L. M. Redman, *Ind. Eng. Chem.*, **40**, 1190 (1948).

hydrocarbons in only 57 to 60% yield. These results might have been anticipated since it might have been expected that the hydrocarbons in the product would be lost in the same ratio in which they were formed.

The general technique in conducting reactions with sodium was as follows. The apparatus was swept with nitrogen and, while nitrogen passed through the apparatus, solvent (250 ml.), salt (0.1 mole) and sodium (0.5 g. atom) were added through a side neck of the Morton flask. The side neck was then closed with a thermometer well. The solvent was heated to the boiling point within about 10 minutes by means of a Glascol heating mantle and then the stirrer was started. Stirring was commenced slowly at first until the speed of the reaction could be judged and then, if the reaction were not excessively fast, was increased to just below the maximum speed possible (motor run at 90–100 volts). The reaction time as recorded in Tables I and II was the time interval between when the stirrer was started and stopped. A reaction was deemed complete when bubbles of gas ceased to pass through the scrubbers. For the slow reactions stirring was continued until no more bubbles were seen after 10 or 15 minutes. After the stirrer had been stopped about half of the solvent was distilled rapidly, 125 ml. of fresh solvent was added through a dropping funnel attached to the Claisen head at the top of the Vigreux column, and about half of the solvent was again distilled. The system then was swept with from 6 to 8 liters of nitrogen.

In the early work upon tetramethylammonium chloride and allyltrimethylammonium chloride the solid salt (contained in a flask attached to one neck of the Morton flask by wide diameter rubber tubing) was added in increments over a period of four hours to the finely divided sodium.

The yield of "volatile" amine (predominantly trimethylamine) was obtained by titration of the contents of the gas scrubbers with sodium hydroxide to a methyl red end-point. For tetramethyl- and tetraethylammonium bromide (Table I) and triethylmethylammonium chloride (Table II), the dioxane distillate was combined with the contents of the gas scrubbers before titration in order to give more nearly the total yield of amine.

Ethyldimethylamine was detected in the amines from the reaction of tetramethylammonium bromide with sodium by conversion of the amines into their methiodides. These were then converted into the corresponding quaternary ammonium hydroxides, which were subjected to pyrolysis to give ethylene in low yield as qualitatively identified by infrared absorption and measured volumetrically as described below for unsaturated hydrocarbons.

The analysis of hydrocarbons from a reaction was accomplished as follows. A gas sample was brought into the gas buret of an Orsat apparatus, and the contraction in volume upon passing the gas sample repeatedly through 22% mercuric sulfate in 22% sulfuric acid was measured in order to determine the total amount of olefin[29] present. The olefin so determined is recorded in Tables I and II. The gas sample was next passed into a gas bubbler containing concentrated sulfuric acid in order to remove water vapor. The gas sample was then transferred to an evacuated gas cell which was a 10-cm. open path cell with rock salt windows. Successive samples were similarly transferred to the gas cell until the desired pressure was attained as recorded by a mercury manometer. The temperature of the gas was recorded and the total pressure in the cell was brought to one atmosphere with nitrogen gas. The cell was placed in the spectrophotometer (a Perkin–Elmer, model 21 recording infrared spectrophotometer with rock salt prisms) and scanned from 2 to 14 μ to confirm removal of all unsaturates and to identify the saturated gases qualitatively. For quantitative analysis optical density measurements were then made at predetermined wave lengths as follows: methane, 7.69 μ; ethane and propane, 3.45 and 6.82 μ; *n*-butane, 3.45 and 6.84 μ; isobutane, 6.79 and 8.54 μ. For ethane, propane and *n*-butane the wave length near 3.45 μ was the principal absorption band used for analysis, the wave length near 6.8 μ being used as a check band for the more concentrated samples of alkane. Empirical calibration curves of optical density *versus* partial pressure were prepared from pure samples of each hydrocarbon (the total pressure was always brought to one atmosphere by addition of nitrogen). These calibration curves were generally nearly linear over the range of partial pressures used for analyses save for the curve for methane. Suitable corrections were applied for the absorption of methane in the region of the higher alkane and *vice versa*. The perfect gas laws were assumed to hold for all of the gases under the conditions of the analyses. The general validity of the analytical method used was tested by analyses upon synthetic methane–alkane mixtures of known composition. These measurements and the average deviation from the mean of optical density measurements were used to estimate the probable limits of error in each analysis as shown in Table II.

To analyze for the individual unsaturated components, the gas from the sodium reaction was dried by passage through a foot-long tube filled with Drierite (a large enough sample being used to flush the air out of the Drierite) and thence into the evacuated gas cell. This sample was scanned from 2 to 14 μ on the same optical density paper which had been used to scan the hydrocarbon sample from which unsaturates had been removed. By using this previous scan as a reference line, unsaturates could be qualitatively identified and estimated semi-quantitatively with the help of calibration curves. Ethylene was analyzed at 10.54 μ, butene-1 at 6.12 and 10.97 μ and isobutylene at 11.25 μ. Acetylene was qualitatively identified by its band at 13.67 μ. Some of the results from these analyses are as follows: *t*-butyltrimethylammonium iodide with sodium in dioxane gave a total olefin of 5.3 ± 0.7% which consisted of 1.8% isobutylene, 2.0% ethylene and 1.5 ± 1.1% of acetylene (estimated by difference); *n*-butyltrimethylammonium iodide gave a total olefin of 21.5 ± 1.1% which consisted of 20.2% butene-1, 0.7% ethylene and a trace of acetylene; *sec*-butyltrimethylammonium iodide gave a total olefin of 19.2 ± 1.0% which consisted of 11.8% butene-1, 2.2% ethylene and by difference 5.2% of butene-2 with a trace of acetylene.

The olefin from the reaction of allyltrimethylammonium chloride with sodium was identified qualitatively as propylene by addition of bromine to give propylene bromide (b.p. 141° at 740 mm. and $n^{20}\text{D}$ 1.5203) which was converted to an isothiourea picrate of m.p. 252°. Since the recorded melting point[30] of the isothiourea picrate of propylene bromide is 232°, the preparation of this derivative was repeated once using propylene bromide from Eastman Kodak Co., and another time using propylene bromide which we had prepared from propylene obtained from dehydration of purified isopropyl alcohol; each preparation gave an isothiourea picrate of m.p. 252°.

The following test was made to see if tri-*n*-butylamine underwent cleavage by sodium in dioxane under the usual reaction conditions to give volatile hydrocarbon. Tri-*n*-butylamine (0.098 mole) and sodium (0.50 g. atom) were stirred for 16 minutes in 250 ml. of dioxane at reflux. The system was swept with nitrogen. The sweep gas was found to contain no saturated or unsaturated hydrocarbons by the methods of analysis given above.

Reaction of Ammonium Halides with Sodium in *t*-Amyl Alcohol–Dioxane.—These reactions were carried out in the same manner as those described above in solvent dioxane except that the present solvent consisted of 140 ml. of *t*-amyl alcohol plus 110 ml. of dioxane. Because of the products which resulted from the reaction of *t*-amyl alcohol with sodium (see below), infrared analyses for hydrocarbon were unreliable and are not reported. The amines produced in these reactions were identified and provide some confirmation of the general scheme of cleavage in dioxane as reported in Tables I and II. In all cases the amines produced were characterized by the melting point of the corresponding picrate and by mixed melting point with a known sample of the picrate.

Tetramethylammonium chloride (see Table I) gave 80.2% yield of amine in which only trimethylamine was identified.

n-Butyltrimethylammonium chloride in 43 minutes reaction time gave 48.4% yield of olefin and 77% yield of total amines. The volatile amine was characterized as trimethylamine while the amine which co-distilled with the solvent was a mixture of trimethylamine and *n*-butyldimethylamine.

Di-*n*-butyldimethylammonium chloride in 28 minutes reaction time gave 74% yield of olefin (butene-1 according to its infrared spectrum). The reaction mixtures from several such runs (with a total of 0.240 mole of chloride) were combined and worked up by extraction and distillation procedures to give (with some loss of the more volatile amine) 14.4

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(29) A. W. Francis and S. J. Lukasiewicz, *Ind. Eng. Chem., Anal. Ed.*, **17**, 703 (1945).

(30) W. J. Levy and N. Campbell, *J. Chem. Soc.*, 1442 (1939).

g. of *n*-butyldimethylamine (b.p. 91–94°), 1.0 g. of intermediate fraction and 5.2 g. (15% yield) of di-*n*-butylmethylamine (b.p. 161–162.5°). The picrate of di-*n*-butylmethylamine has m.p. 86.6–87.4°.

Tri-*n*-butylmethylammonium iodide, in a reaction so vigorous after one minute of stirring that, even though stirring had been stopped, half of the reaction mixture was forced over into the distillation receiver where reaction continued in absence of stirring or heating, gave 5% yield of olefin. Tri-*n*-butylmethylammonium bromide, in a reaction somewhat less vigorous than that of the iodide, gave 17% yield of olefin. The reaction mixtures from 0.208 mole of the iodide and 0.155 mole of the bromide were combined and worked up by extraction and distillation procedures to give at 740 mm. 5.8 g. forerun (b.p. 100–162°), 5.4 g. (11% yield) of di-*n*-butylmethylamine (b.p. 161–162.5°), 1.9 g. of intermediate fraction and 43.7 g. (65% yield) of tri-*n*-butylamine (b.p. 212–213°).

Tetra-*n*-butylammonium bromide upon starting the stirrer gave such vigorous reaction that some 40% of the reaction mixture foamed over into the safety flask where reaction apparently stopped. The yield of olefin was 21% (in two other runs which were better controlled the yield of olefin averaged 50%) and from the reaction mixture 55% yield of tri-*n*-butylamine was isolated. The olefin from several such runs was combined and treated with bromine to give a dibromide of b.p. 164.0–164.5° at 738 mm. (1,2-dibromobutane[31] has b.p. 166°).

Reaction of Tetra-*n*-butylammonium Bromide with Sodium *t*-Amyloxide.—Sodium (0.50 g. atom) was stirred with 140 ml. of *t*-amyl alcohol and 110 ml. of dioxane at the boiling point until hydrogen ceased to be evolved (190 minutes reaction time) and then 28 g. (0.087 mole) of tetra-*n*-butylammonium bromide was added over a period of one hour to the refluxing mixture. After an additional half-hour, stirring was stopped. The yield of olefin was 76% (some of the bromide stuck to the walls of the container during addition and thereby escaped reaction). The olefin was characterized as butene-1 by preparation of its dibromide.

Test for Decomposition of Tri-*n*-butylmethylammonium Iodide in Boiling Dioxane-*t*-Amyl Alcohol.—The apparatus was the same as that described for the sodium reactions above except that the usual bubblers containing hydrochloric acid were replaced by a bubbler filled with 170 ml. of 95% ethyl alcohol containing 0.02 mole of silver nitrate. Tri-*n*-butylmethylammonium iodide (0.081 mole), 140 ml. *t*-amyl alcohol and 110 ml. of dioxane were placed in the reaction flask. The mixture was heated to boiling, stirring was commenced, and 100 ml. of solvent was distilled from the reaction flask over a period of one hour. The system was then swept with nitrogen. No precipitate was visible in the alcoholic silver nitrate. The distillate was combined with the alcoholic silver nitrate; no precipitate formed after several minutes of shaking. A 5-ml. portion of the silver nitrate solution was treated with one drop of methyl iodide; a yellow precipitate was formed after one minute. A 10-ml. portion of the solution was mixed with distilled water and allowed to stand overnight, but no precipitate formed.

Reaction of *t*-Amyl Alcohol with Sodium.—Sodium (0.50 g. atom) was stirred with 140 ml. of *t*-amyl alcohol and 110 ml. of dioxane at reflux for 30 minutes by which time no more gas was evolved. The gaseous product was partially absorbed by mercuric sulfate–sulfuric acid solution (1.2% yield of olefin based on sodium). The product had an absorption band at 6.8 μ of an intensity corresponding to 4.9% yield, if it were *n*-butane (based on sodium with the assumption that 2 g. atoms of sodium yield one mole of product). These products of reaction were shown not to be dioxane or *t*-amyl alcohol vapors on the basis of their infrared spectra. Moreover, the material remaining after passage through mercuric sulfate solution was definitely not *n*-butane, *n*-pentane or isopentane; its infrared spectrum was similar to that recorded[32] for 2,2-dimethylbutane. The same products, but in somewhat higher yield, were obtained by reaction of sodium with *t*-amyl alcohol alone. The gaseous products from the reaction of 700 ml. of *t*-amyl alcohol with 27 g. of sodium were passed through a trap cooled with Dry Ice–acetone. A liquid (4.2 ml.) was collected in the cold trap; three-fourths of this liquid upon simple distillation boiled from 42 to 53° and thus some of the product may indeed have been 2,2-dimethylbutane (b.p. 49.7°). It is concluded that impurities in the *t*-amyl alcohol are probably responsible for the products other than hydrogen obtained upon reaction with sodium.

Reaction of Dioxane with Sodium and Potassium.—Sodium–potassium alloy (prepared from 15 g. of potassium and 5 g. of sodium) was stirred in 250 ml. of refluxing dioxane in the apparatus described above for cleavage of quaternary ammonium halides. No reaction was evident after 75 minutes; therefore 15 ml. of a 2% by volume solution of oleic acid in dioxane was added over a period of 20 minutes. After two hours of stirring the alloy appeared to be well dispersed in the solvent. After four hours gas evolution began such that 500 ml. was evolved during the next hour. In an attempt to accelerate the reaction 50 ml. of a 2% by volume solution of isopropyl alcohol in dioxane was added over a period of 90 minutes. After 12 hours of stirring one liter of gas had been collected. The reaction was stopped overnight and then stirring at reflux was continued on the next two days. The sodium–potassium alloy coalesced after 24 hours of stirring. Analysis of the gaseous product by absorption in mercuric sulfate–sulfuric acid solution indicated that 824 ml. (S.T.P.) of an olefinic product had been evolved. The olefin was identified as ethylene by conversion to ethylene dibromide. The yield of ethylene was 19% on the basis that 2 g. atoms of potassium give one mole of ethylene. The sodium-potassium alloy remaining in the reaction flask was decomposed with absolute ethanol and the contents made slightly acidic with anhydrous hydrogen chloride. After filtration the liquid was distilled through a three-foot column until a pot temperature of 108° was attained whereupon about 50 ml. of liquid remained. An attempt then was made to distil this liquid through a short column *in vacuo;* however at pot temperatures which did not exceed 140° the flask residue seemed to pyrolyze to a carbonaceous mass which was insoluble in all common solvents tried. The column contained a little of a white solid of m.p. 70–130°. The column was rinsed with water; the water washing gave a positive periodic acid test for a 1,2-glycol. In a reaction (to be described in detail elsewhere) between sodium-potassium alloy and 3-chloropropyltrimethylammonium chloride in dioxane, 1070 ml. (S.T.P.) of ethylene appeared in the gaseous product and the reaction mixture when worked up as above gave 0.3 ml. of a liquid of b.p. *ca.* 90° at 14 mm. This liquid gave a 3,5-dinitrobenzoate of m.p. 173–174°. The 3,5-dinitrobenzoate of a known sample of ethylene glycol had m.p. 173.5–174.5° and gave no depression of melting point upon admixture with the unknown dinitrobenzoate.

An attempt to treat dioxane (250 ml.) with sodium (10 g.) under conditions similar to that above with sodium–potassium alloy gave no appreciable evolution of gas in 12 hours beyond that expected from the isopropyl alcohol and oleic acid added, and the gases evolved gave no noticeable contraction upon passage through bromine–iodine[33] or concentrated sulfuric acid solutions. In another reaction between sodium (0.70 g. atom) and dioxane which were refluxed with stirring for three hours (no oleic acid or isopropyl alcohol added), the gas obtained by sweeping the system with nitrogen contained a trace of ethylene according to its infrared absorption spectrum. The amount of ethylene was estimated as 0.03% yield on the assumption that 2 g. atoms of sodium yield one mole of ethylene.

***t*-Butyltrimethylammonium Iodide with Sodium in Cumene.**—*t*-Butyltrimethylammonium iodide (0.101 mole) and sodium (0.500 g. atom) were stirred in 250 ml. of freshly purified cumene at 107 ± 8° for 8.5 hours according to the general procedure given above for reaction of ammonium salts in dioxane. The cold reaction mixture was filtered through a fritted glass filter under a nitrogen atmosphere. The filtrate was washed with concentrated sulfuric acid and then water, and was dried over anhydrous calcium sulfate. The filtrate was distilled through a short column to remove cumene and all material volatile up to a bath temperature of 205° (nitrogen atmosphere). The residue was subjected to vacuum sublimation; 0.19 g. of oily crystals was obtained at 0.02 mm. with bath temperatures up to 150°. The oily crystals were resublimed and crystallized from absolute ethanol to give a small amount of material of m.p. 109.4–111.2°.

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(31) I. M. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1943, vol. 1, p. 683.

(32) "Infra-red Spectral Data," American Petroleum Institute Research Project 44.

(33) S. Z. Roginski and F. H. Rathmann, THIS JOURNAL, **55**, 2800 (1933).

The melting point of pure bicumyl[34] is 118.5°. The yield of bicumyl from this run was, therefore, less than 0.19 g. (1.5%). The yields of gaseous products were: isobutane, 17.1 ± 0.5%; methane, 0.96 ± 0.09%; isobutene, 10.8 ± 0.9%; volatile amine, 26.4%.

Attempted Cleavage of *t*-Butyl Methyl Ether with Sodium and Potassium.—The apparatus and procedures used were the same as described above for reaction of ammonium salts in dioxane except that the *t*-butyl methyl ether (0.2–0.3 mole) was added dropwise to the molten alkali metal (0.5 to 0.8 g. atom) with stirring. In dioxane, the reaction was complicated by the fact that the *t*-butyl methyl ether tended to lower the boiling point of the solvent below the melting point of the sodium. No trace of isobutane or isobutylene was detected in 50 minutes of reaction. To overcome the difficulty mentioned, the reaction was run in cumene at about 102°. After stirring for two hours after addition of all the ether, the sodium was destroyed by addition of *t*-butyl alcohol. The infrared spectrum of the gases after removal of any unsaturates contained a rather weak band at 3.45 μ which could indicate a yield of 0.04% of isobutane based on the *t*-butyl methyl ether added.

Reaction of *t*-butyl methyl ether with potassium in dioxane was attempted similarly at the boiling point of the reaction mixture. Since the potassium was not well dispersed, 1.5 ml. of oleic acid was added, but still the particle size was large. After three hours reaction time a maximum of 0.01% (if any) of isobutane was formed. The reaction next was attempted with potassium in boiling tetrahydrofuran. After one hour, although the potassium appeared well dispersed, there was no sign of reaction. Anthracene (0.1 g.) then was added to see whether reaction could be induced. After 54 minutes the reaction mixture, by this time of a deep blue color, was decomposed with *t*-butyl alcohol. There was no evidence of any isobutane in the gases swept out of the system with nitrogen.

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[34] P. Bryce-Smith, *J. Chem. Soc.*, 1712 (1955); 1603 (1956).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

Carbanions. III. Cleavage of Tetraalkylammonium Halides by Sodium in Liquid Ammonia[1]

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Tetraalkylammonium halides are cleaved rapidly by sodium in liquid ammonia at −33° to give alkane and tertiary amine and, in an accompanying elimination reaction with sodamide, alkene and tertiary amine. Ammonium halides of the type $R_n(CH_3)_{4-n}NX$ give RH and CH_4 in the following ratios after statistical correction for unequal numbers of groups and multiplication by 100: Et, 0.83 ± 0.06; *n*-Bu, 0.89 ± 0.29 < *n*-Pr, 1.69 ± 0.12 < *i*-Pr, 13.7 ± 0.8 < *s*-Bu, 43.8 ± 2.1 < Me, 100 < *t*-Bu, 75,000 ± 18,000. These ratios for cleavage of groups follow about the same order as those obtained previously with sodium in refluxing dioxane, although the cleavages at the lower temperature of boiling liquid ammonia are more selective. Possible mechanisms for these reductive cleavages are discussed and it is concluded that methyl and the higher primary alkyl groups probably cleave from nitrogen as carbanions while secondary and tertiary alkyl groups predominantly cleave as free radicals. While the relative rates of cleavage are primarily due to the stabilizing or destabilizing effect of α-alkyl groups upon incipient carbanions or radicals in the transition state for cleavage, secondary and especially tertiary alkyl groups are assisted by steric acceleration. A case is discussed in which steric acceleration appears to be the dominant factor governing relative rates of cleavage. Aryltrimethylammonium ions, under the usual conditions of the Emde reduction, appear to cleave aryl and methyl groups by way of transition states possessing appreciable carbanion-like character. The very slow cleavage of *t*-butyl methyl ether by sodium or potassium is discussed.

The previous paper in this series[2] dealt with the cleavage of tetraalkylammonium halides by sodium in dioxane, *t*-amyl alcohol–dioxane mixture and cumene. These reactions obviously were heterogenous since sodium is not visibly soluble[3] in these media and the ammonium salts were frequently almost insoluble. In the present paper cleavage is studied with solutions of sodium in liquid ammonia in order to obtain data under more nearly homogeneous conditions.

The reaction of tetramethylammonium iodide with a solution of potassium in liquid ammonia was first investigated by Thompson and Cundall[4]; the products at room temperature were reported to be trimethylamine, ethane and potassium iodide. Schlubach and Ballauf[5] found that tetraethylammonium chloride with potassium in liquid ammonia gave triethylamine. They presumed that the reaction was

$$2K + 2(C_2H_5)_4NCl = 2KCl + C_4H_{10} + 2(C_2H_5)_3N$$

but they obtained considerably more gas than predicted by this equation.

More recently Birch[6] reported that phenyltrimethylammonium iodide was cleaved by sodium in liquid ammonia containing *t*-amyl alcohol to give benzene (51% yield) and trimethylamine. Benzyltrimethylammonium iodide similarly gave toluene and trimethylamine. Birch noted that the use of sodium in liquid ammonia was a powerful variant of the usual Emde reduction with sodium amalgam. Similarly Clayson[7] has reported the cleavage of some tetrahydroisoquinolinium iodides with sodium in liquid ammonia containing 5% ethanol and also in absence of eth-

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[1] Abstracted in part from the Ph.D. thesis of R. W. Stevenson, Georgia Institute of Technology, May, 1958.

[2] Paper II, E. Grovenstein, Jr., E. P. Blanchard, Jr., D. A. Gordon and R. W. Stevenson, THIS JOURNAL, **81**, 4842 (1959).

[3] The recent report [J. L. Down, J. Lewis, B. Moore and G. Wilkinson, *Proc. Chem. Soc.* (*London*), 209 (1957)] that potassium dissolves in tetrahydrofuran to give a blue solution prompts us to report our experience with this system. While potassium added to commercial tetrahydrofuran gives various colors, we (with Mr. L. P. Williams, Jr.) find that tetrahydrofuran which has been refluxed one hour over potassium with vigorous stirring and then distilled from potassium gives no visible color when treated with potassium even at the boiling point when observed in two-liter quantities.

[4] C. M. Thompson and J. T. Cundall, *J. Chem. Soc.*, **53**, 761 (1888).

[5] H. H. Schlubach and F. Ballauf, *Ber.*, **54**, 2811 (1921).

[6] A. J. Birch, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 245 (1949); *C. A.*, **46**, 2520, 11117 (1952).

[7] D. B. Clayson, *J. Chem. Soc.*, 2016 (1949).