

The melting point of pure bicumyl³⁴ 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.

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

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

Carbanions. III. Cleavage of Tetraalkylammonium Halides by Sodium in Liquid Ammonia¹

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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 $R_n(CH_2)_{4-n}NX$ 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 series² dealt with the cleavage of tetraalkylammonium halides by sodium in dioxane, *t*-amyl alcohol–dioxane mixture and cumene. These reactions obviously were heterogeneous since sodium is not visibly soluble³ 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 Cundall⁴;

the products at room temperature were reported to be trimethylamine, ethane and potassium iodide. Schlubach and Ballauf⁵ found that tetraethylammonium chloride with potassium in liquid ammonia gave triethylamine. They presumed that the reaction was



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

More recently Birch⁶ 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 Clayson⁷ has reported the cleavage of some tetrahydroisoquinolinium iodides with sodium in liquid ammonia containing 5% ethanol and also in absence of eth-

(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).

anol. Thus 2,2-dimethyl-1,2,3,4-tetrahydroisoquinolinium iodide gave dimethyl-2-*o*-tolylethylamine in some 70% yield. The methiodide of dimethyl-2-(3',5'-dimethoxy-2'-methylphenyl)-ethylamine similarly gave 2,4-dimethoxy-6-ethyltoluene in unspecified yield.

In contrast to earlier reports, Jolly⁸ found that sodium and tetraethylammonium bromide in liquid ammonia at the boiling point gave a mixture of gases which when freed from amine contained 42.1% ethylene, 56.8% ethane and 1.0% hydrogen. Ethylene was shown to be produced by the ready reaction of potassium amide upon tetraethylammonium bromide in liquid ammonia at -75° .

After the present work was underway, Hazlehurst, Holliday and Pass⁹ reported that tetraethylammonium chloride reacted with potassium in liquid ammonia at -78° to give triethylamine and variable ratios, under apparently similar conditions, of ethane to ethylene. Tetramethylammonium chloride, bromide and iodide similarly gave trimethylamine, methane, a "trace" of ethane and a probable "trace" of ethylene. Tetramethylammonium chloride reacted with potassium amide at -78° in a very slow reaction to give evidently trimethylamine and methylamine, while in one such experiment a little ethylene was found as well. Tetra-*n*-propylammonium chloride with potassium in liquid ammonia (at -78°) gave tri-*n*-propylamine, propane and propylene; triethylmethylammonium chloride gave triethylamine, diethylmethylamine, methane, ethylene and a "trace" of ethane; tri-*n*-propylmethylammonium chloride gave tri-*n*-propylamine, di-*n*-propylmethylamine, methane, propylene and a "trace" of ethane but no propane was reported; triethylammonium chloride gave triethylamine and hydrogen (only). The order of ease of reductive fission of groups was, therefore, $H > CH_3 > C_2H_5$ or $n-C_3H_7$.

Experimental Details

The ammonium halides used were made by the procedures reported earlier.² Anhydrous ammonia (99.9% minimum purity) was from Matheson Co., Inc., and was distilled from the cylinder into the reaction vessel without additional purification.

The apparatus used for carrying out reactions in liquid ammonia was similar to that described by Johnson and Fernelius¹⁰ except that safety traps were placed in the line on either side of the reaction vessel and the cooling bath of liquid ammonia was omitted. The reaction vessel was a tube 3 cm. in diameter by 28 cm. tall and had a small diameter tube leading to the bottom; through this small tube ammonia gas could enter and keep the reaction mixture stirred. Near the top of the reaction vessel were attached two 19/38 outer joints. These joints were fitted to small retorts which were of such design that by rotation their contents dropped into the reaction vessel. In one retort was placed quaternary ammonium salt. The retort with its salt after drying *in vacuo* at 70 to 85° overnight or longer, was closed with a rubber stopper and weighed and then stored in a desiccator over phosphorus pentoxide until ready for reaction. In the other retort was placed sodium which was cut into one or two pieces and weighed just before reaction. The retort containing ammonium salt usually was reweighed after reaction to give the weight of salt added since often some of the salt stuck to the walls. Sometimes a little salt stuck

in the neck or top of the reaction tube and did not come into contact with the liquid ammonia solution. No correction could be made for this, but an excess of salt was ordinarily added and the yields were calculated on the basis of the sodium added. In Table III the sum of the yields of hydrocarbons and olefin from ethyl and isopropylammonium halides averages 90% if the yields are calculated on the basis of ammonium halide taken; therefore, on the average at least 90% of the ammonium halide must have been transferred to the site of reaction.

The general procedure for conducting a reaction in liquid ammonia was as follows. Gaseous ammonia was swept through the system until all air had been transferred to the gas collection chamber. The gas collection chamber was refilled with fresh brine. Ammonia was again allowed to enter the system, quaternary ammonium salt was added to the reaction vessel by rotating the appropriate retort, and a Dry Ice-acetone-bath was placed about the reaction vessel to liquefy the ammonia gas. After 50 ± 10 ml. of liquid ammonia had been collected, the Dry Ice-acetone-bath was removed. As the system warmed to its boiling point, qualitative observations concerning the solubility of the salt in liquid ammonia were made. The ammonia stream was reduced during the warming such that a constant slow stream of ammonia bubbled through the liquid ammonia so as to prevent bumping when the boiling point was obtained. When the ammonia had come to a boil sodium was added by tipping the second retort. The time of reaction as given in the tables was the time required for discharge of the blue color of sodium dissolved in liquid ammonia or, if sodium was in excess, it was the time required for evolution of gases which were insoluble in brine to cease or to appear to cease. Reaction times (not recorded) for Table III were most commonly three to ten minutes. The hydrocarbon gases generated were swept into the collection chamber by gaseous ammonia. Fresh brine was added to the collection chamber as required. The liquid ammonia solution was allowed to evaporate slowly with continued stirring by a slow stream of ammonia. Evaporation of the last 5 to 10 ml. of liquid ammonia was accelerated by cautious warming of the reaction vessel with a beaker of cold water. After all the liquid ammonia had evaporated, the system was swept rather rapidly for a few minutes with gaseous ammonia.

The gaseous products were transferred quantitatively to a Orsat gas apparatus and were bubbled through a saturated brine solution which was one molar in hydrochloric acid until constant volume was attained. The volume of gas evolved in the reaction then was measured. The olefins were removed by absorption in mercuric sulfate-sulfuric acid solution and the saturated hydrocarbons analyzed by infrared absorption by the procedures described previously.² Because of the small size of the gaseous product, the identity of the olefinic product was generally not checked by its infrared spectrum.

In preliminary experiments the order of addition of reactants was reversed, *i.e.*, ammonium salt was added to a solution of sodium in liquid ammonia. The salt, however, was necessarily added before the ammonia came to its boiling point, since otherwise extreme bumping occurred and the reaction mixture could not be contained in the reaction tube. These experiments gave irreproducible results for the alkane to methane ratio doubtless because of the variable temperatures at which reaction occurred.

All but a few of the quaternary ammonium halides used in the present work were soluble in boiling liquid ammonia at the concentrations normally employed (0.06 *M*). Very crudely estimated solubilities (from visual observations of the apparent fraction of salt which dissolved) of those salts which were not completely soluble at the concentration employed are as follows: tetramethylammonium bromide, "insoluble"; tetra-*n*-propylammonium bromide, 0.05 mole per liter; *t*-butyltrimethylammonium iodide, 0.002 mole per liter.

Unless otherwise indicated, all reactions given in the tables were run at the boiling point of liquid ammonia. Since the pressure within the reaction vessel was 760 ± 10 mm. and since the concentration of reactants was low, the reaction temperature must correspond essentially to that of the normal boiling point of pure ammonia (-33.4°). In the reactions of Table III 0.0030 ± 0.0005 mole of quaternary ammonium salt and 0.0050 ± 0.0005 g. atom of sodium were used; therefore ammonium salt was generally in excess and yields were calculated on the basis of sodium except in the

(8) W. J. Jolly, *This Journal*, **77**, 4958 (1955).

(9) D. A. Hazlehurst, A. K. Holliday and G. Pass, *J. Chem. Soc.*, 4653 (1956).

(10) W. C. Johnson and W. C. Fernelius, *J. Chem. Educ.*, **6**, 445 (1929).

TABLE I

PRODUCTS FROM REACTION OF SIMPLE TETRAALKYLAMMONIUM HALIDES WITH SODIUM IN LIQUID AMMONIA

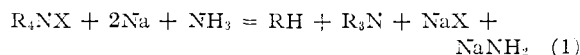
Ammonium halide R ₄ NBr	Mole	Sodium, g. atom	Time, min.	Yield, % ^a	
				Alkane	Alkene
Me ₄ NBr	0.00494	0.00614	120	90.6
Me ₄ NBr ^b	.0100	.00430	70	94.4 ± 1.5	0.1 ± 0.4
Et ₄ NBr ^c	.00294	.0062	..	57.5	36.2
Et ₄ NBr	.0109	.00445	35	88.6 ± 1.2	84.8 ± 0.7
<i>n</i> -Pr ₄ NBr	.0101	.00429	5	76.3 ± 1.4	38.5 ± 0.6
<i>n</i> -Pr ₄ NBr	.00945	.00450	4	83.7 ± 1.0	36.4 ± 1.8
<i>n</i> -Bu ₄ NBr ^c	.00299	.00587	12	79.2	2.9
<i>n</i> -Bu ₄ NBr	.0100	.00442	11	89.5 ± 1.0	40.3 ± 1.0

^a Yields based on sodium unless otherwise indicated.

^b No ethane was detectable by infrared analysis. Since Phillips Petroleum Co. estimates that 0.11% of ethane was in the methane used for infrared calibrations, 0.1 ± 0.1% of ethane may have been present. ^c Yields based on ammonium halide.

Discussion of Results

In Tables I, II and III are presented the yields of hydrocarbons from the reaction of tetraalkylammonium halides with sodium in liquid ammonia. Yields are reported on the basis of ammonium halide or, more frequently, sodium in accordance with which was present in the lesser amount as given by the equation



When yields are reported on the basis of sodium, alkene yields are reported as though two moles of sodium are required to produce one mole of alkene. This method of calculation was adopted in order to report alkene and alkane yields on the same

TABLE II

EFFECT OF REACTION CONDITIONS UPON PRODUCT COMPOSITION FROM QUATERNARY AMMONIUM HALIDES WITH SODIUM IN LIQUID AMMONIA

Halide, mole	Sodium, g. atom	Time, min.	Yield, % ^a			Observed ratio 100(RH/CH ₄)
			CH ₄	RH	Alkene	
Tri- <i>n</i> -butylmethylammonium bromide, R ₃ CH ₂ NBr						
0.00298	0.00484	2	94.7 ± 1.8	1.88 ± 0.05	8.3 ± 0.5	1.98 ± 0.09
.00284	.00495	4	95.5 ± 2.4	2.01 ± .08	2.7 ± 0.2	2.10 ± .14
.000985	.00484	..	85 ± 3	1.76 ± .06	0.8 ± 1.6	2.05 ± .15 ^b
.00293	.00166	2	92.1 ± 1.6	1.80 ± .08	46.0 ± 1.9	1.95 ± .12
.00102	.00140	1	96.3 ± 1.3	1.73 ± .12	15.8 ± 2.0	1.80 ± .15
.00171	.00151	136	58.8 ± 0.8	0.25 ± .10	16.0 ± 1.6	0.43 ± .18 ^c
.00298	.00477	79	40.1 ± 0.8	0.16 ± .04	28.1 ± 1.1	0.40 ± .11 ^d
<i>sec</i> -Butyltrimethylammonium iodide, R(CH ₃) ₃ NI						
0.00303	0.00591	3	67.1 ± 1.1	10.0 ± 0.3	4.1 ± 0.3	14.9 ± 0.7
.00301	.00484	10	59.1 ± 1.5	8.5 ± .2	8.7 ± 0.3	14.3 ± .7
.00214	.00417	115	17.8 ± 0.7	1.66 ± .07	31.1 ± 2.5	9.3 ± .8 ^d
.00287	.00467	260	17.1 ± 0.4	1.43 ± .05	34.5 ± 1.1	8.4 ± .5 ^d

^a Yields based on sodium unless otherwise indicated. ^b Yield based on ammonium halide. ^c Reaction run at temperature of Dry Ice-acetone-bath, -78°. ^d Reaction run at temperature of Dry Ice-ethanol-bath, -72°.

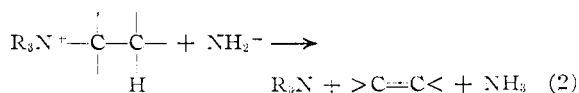
cases indicated otherwise. Some variations from these standard conditions are indicated in Tables I and II.

Test for Reduction of Butene-1 and Isobutylene.—Butene-1 (0.002 mole) and ammonia (50 ml.) were condensed at Dry Ice temperature in the apparatus for cleavage of ammonium salts, sodium (0.006 g. atom) was added, and the reaction mixture allowed to boil in the usual way until all ammonia had evaporated. The gaseous products after removal of butene-1 had a weak infrared absorption band at 3.46 μ. This band indicated the presence of 0.6 ± 0.3% of *n*-butane in the butene-1 from the treatment with sodium. A sample of the original butene-1 when subjected to the same analysis was found to contain 0.21 ± 0.05% of *n*-butane. Therefore little, if any, butene-1 was reduced to butane under the usual reaction conditions.

A similar experiment with isobutylene and sodium in liquid ammonia gave 0.15 ± 0.02% of isobutane in the isobutylene from the treatment with sodium. A sample of the original isobutylene contained 0.10 ± 0.04% isobutane. Therefore no significant reduction occurred.

***t*-Butyl Methyl Ether with Sodium.**—In the apparatus described above for cleavage of ammonium halides, 40 ml. of liquid ammonia was condensed and then 5.0 ml. (0.043 mole) of *t*-butyl methyl ether and 0.120 g. (0.0052 g. atom) of sodium were added. The ether was not miscible with the solution of sodium in liquid ammonia. The mixture was held just below its boiling point for 31 minutes and then was allowed to evaporate in the usual manner. Most of the sodium reacted during this procedure. The gaseous product, after treatment with mercuric sulfate-sulfuric acid and then concentrated sulfuric acid, showed on infrared analysis from 2 to 15 μ one band of medium intensity at 3.46 μ which could correspond to 0.85 ± 0.05% yield of isobutane based on sodium or 0.051% based on ether.

basis. Olefin doubtlessly arises from the reaction of amide ion upon quaternary ammonium halide according to the process^{8,9}



If sodamide is produced only by equation 1, then the yield of olefin can equal but not exceed the yield of alkane. Such a high yield of olefin can be attained only if the reaction 2 proceeds at a rate equal to that of reaction 1 or if at least one mole of ammonium halide is added for each gram atom of sodium. In Table III where only 0.03 mole of ammonium halide and 0.05 g. atom of sodium were allowed to react the yield of olefin is generally considerably less than that of alkane and thus reaction 1 proceeds faster than 2 under the present conditions where initially no sodamide was present. On the other hand, where a large excess of ammonium halide over sodium was allowed to react, as in some of the reactions of Table I, the yield of olefin sometimes approached that of alkane. In only two of the reactions reported in the tables is the yield of olefin greater than that of alkane, namely in the slow reaction of *sec*-butyltrimethylammonium iodide with sodium at -72° (Table II).

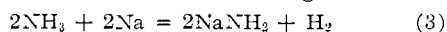
TABLE III

PRODUCTS FROM REACTION OF QUATERNARY AMMONIUM HALIDES, $R_n(\text{CH}_3)_{4-n}\text{NX}$, WITH SODIUM IN LIQUID AMMONIA

Ammonium halide $R_n(\text{CH}_3)_{4-n}\text{NX}$	Yield, % ^a			Observed ratio 100(RH/CH ₄)	Corrected ratio $100\left(\frac{4-n}{n}\right)(\text{RH}/\text{CH}_4)$
	CH ₄	RH	Alkene		
<i>n</i> -Bu ₃ (CH ₃)NI	98.2 ± 1.4	2.05 ± 0.02	0.7 ± 0.3	2.09 ± 0.05	0.70 ± 0.02
<i>n</i> -Bu ₃ (CH ₃)NI ^b	87.0 ± 2.0	1.93 ± .02	0.7 ± .3	2.22 ± .07	.74 ± .02
<i>n</i> -Bu ₂ (CH ₃) ₂ NBr	90.2 ± 1.6	0.81 ± .04	0.6 ± .2	0.90 ± .06	.90 ± .06
<i>n</i> -Bu ₂ (CH ₃) ₂ NBr	72.4 ± 1.8	.64 ± .07	0.4 ± .2	.88 ± .11	.88 ± .11
<i>n</i> -Bu(CH ₃) ₃ NI	98.0 ± 1.6	.27 ± .03	2.4 ± .4	.28 ± .04	.84 ± .12
<i>n</i> -Bu(CH ₃) ₃ NI	94.5 ± 1.9	.30 ± .03	1.0 ± .3	.32 ± .04	.96 ± .12
<i>n</i> -Bu(CH ₃) ₃ NBr	90.4 ± 1.0	.33 ± .02	0.8 ± .3	.36 ± .03	1.08 ± .09
<i>n</i> -Bu(CH ₃) ₃ NBr	87.5 ± 1.4	.38 ± .03	0.5 ± .3	.43 ± .04	1.29 ± .12
<i>n</i> -Bu(CH ₃) ₃ NCl	98.0 ± 2.3	.31 ± .03	0.7 ± .3	.32 ± .04	0.96 ± .12
<i>n</i> -Bu(CH ₃) ₃ NCl	96.3 ± 1.9	.34 ± .03	1.4 ± .3	.35 ± .04	1.05 ± .12
<i>t</i> -Bu(CH ₃) ₃ NI	0.36 ± 0.11	72.4 ± 1.6	1.8 ± .5	21,000 ± 6000	63,000 ± 18,000
<i>t</i> -Bu(CH ₃) ₃ NI	0.30 ± 0.06	88.0 ± 2.0	8.2 ± .6	29,000 ± 6000	87,000 ± 18,000
Et ₃ (CH ₃)NI	69.7 ± 1.8	1.65 ± 0.06	41.8 ± .5	2.40 ± 0.15	0.80 ± 0.05
Et ₃ (CH ₃)NI	71.0 ± 1.6	1.71 ± .07	42.3 ± .4	2.40 ± .15	.80 ± .05
Et ₃ (CH ₃)NBr	53.0 ± 1.5	1.35 ± .07	30.9 ± .3	2.56 ± .20	.85 ± .07
Et ₃ (CH ₃)NBr	67.9 ± 1.7	1.61 ± .07	39.1 ± .4	2.36 ± .16	.79 ± .05
Et ₃ (CH ₃)NCl	76.3 ± 1.5	2.02 ± .07	53.2 ± .5	2.65 ± .15	.88 ± .05
Et ₃ (CH ₃)NCl	58.1 ± 1.2	1.52 ± .07	29.5 ± .3	2.63 ± .18	.88 ± .06
Et(CH ₃) ₃ NI	72.5 ± 1.4	0.10 ± .07	29.9 ± .4	0.14 ± .10	.5 ± .3
Et(CH ₃) ₃ NI	83.7 ± 1.7	0.19 ± .07	31.9 ± .4	0.23 ± .09	.7 ± .3
<i>n</i> -Pr ₃ (CH ₃)NI	94 ± 2	4.51 ± .07	2.2 ± .3	4.78 ± .17	1.59 ± .06
<i>n</i> -Pr ₃ (CH ₃)NI	92.5 ± 2	4.70 ± .15	2.6 ± .6	5.1 ± .3	1.69 ± .09
<i>n</i> -Pr(CH ₃) ₃ NI	95 ± 2	0.57 ± .06	1.2 ± .4	0.60 ± .08	1.8 ± .2
<i>n</i> -Pr(CH ₃) ₃ NI	86.6 ± 1.4	0.49 ± .04	1.9 ± .3	0.56 ± .05	1.68 ± .15
<i>i</i> -Pr(CH ₃) ₃ NI	85 ± 2	3.99 ± .07	21.2 ± .3	4.7 ± .2	14.1 ± .6
<i>i</i> -Pr(CH ₃) ₃ NI ^{b,c}	39.0 ± 1.4	1.68 ± .05	8.5 ± .4	4.3 ± .3	12.9 ± .9
<i>i</i> -Pr(CH ₃) ₃ NBr	90 ± 3	4.05 ± .06	23.8 ± .3	4.5 ± .2	13.5 ± .6
<i>i</i> -Pr(CH ₃) ₃ NBr	93 ± 3	4.38 ± .08	26.1 ± .4	4.7 ± .2	14.1 ± .6

^a Yields based on sodium unless otherwise specified. ^b Yields based on ammonium halide. ^c Some reaction products lost in manipulations.

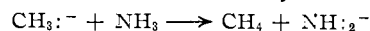
At this low temperature evidently the direct reaction of sodium with ammonia to give sodamide



proceeded at a rate comparable to that of the reductive cleavage (1).

In Table I when comparisons are made at comparable concentrations of reactants, tetraethylammonium bromide gave a higher yield of olefin than tetra-*n*-propyl- or tetra-*n*-butylammonium bromides. This result is to be expected for Hofmann-type elimination.¹¹ Quaternary ammonium halides containing ethyl and isopropyl groups also gave the highest yields of olefin among the compounds reacted in Table III. The low yield of olefin from *t*-butyltrimethylammonium iodide is evidently due to the great speed of the competing reductive cleavage of the *t*-butyl group.

It is significant that tetramethylammonium bromide (Table I) gave no ethylene within experimental error. This indicates, in accord with the discussion in the previous paper of this series,² that methyl carbanions are destroyed by reaction with liquid ammonia before they can initiate the



reactions which have been suggested to explain the formation of ethylene from tetramethylammonium ion with sodium in dioxane. It is significant further than no appreciable ethane was de-

tected in the methane from tetramethylammonium bromide. Hazlehurst⁹ and co-workers have reported a "trace" of ethane from reactions of quaternary ammonium halides containing at least one N-methyl group and they have suggested that the ethane was likely formed by combination of methyl radicals.¹² It is not clear why reactions with potassium in liquid ammonia at -78° or at ordinary temperature⁴ should differ, if indeed they do, from those with sodium at -33° with respect to the formation of ethane. The report¹³ that tetramethylammonium chloride when electrolyzed at a mercury cathode gives tetramethylammonium amalgam which upon heating gives methyl radicals in the gaseous phase, we do not regard as compelling for the concept of methyl radicals in solutions of sodium and potassium in liquid ammonia. Since we found no ethane from tetramethylammonium bromide, we have assumed, in interpretation of our infrared analysis of hydrocarbons from other N-methylammonium halides as reported in Tables II and III, that no ethane was produced unless an N-ethyl group was present.

In Table II the effect of varying the concentration of reactants and the reaction temperature is investigated. For tri-*n*-butylmethylammonium bromide, while the yield of olefin was variable, the ratio of *n*-butane to methane (for convenience

(11) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 429-434.

(12) See also A. K. Holliday and G. Pass, *J. Chem. Soc.*, 3485 (1958).

(13) G. B. Porter, *ibid.*, 760 (1954).

multiplied by 100) was constant at 1.98 within the expected experimental error (here about ± 0.15). On the other hand, lowering the reaction temperature from -33 to -72 or -78° significantly reduced the ratio of butane to methane by a factor of one-fifth. The cleavage reaction is, therefore, more selective at the lower temperature. It should be emphasized that for these reactions, as for most of others reported in this paper, the quaternary ammonium salt was completely dissolved in liquid ammonia but solid pieces of sodium were added to initiate the reaction. The ammonia solution became blue shortly after addition of the sodium, but obviously the dissolution of the sodium was not instantaneous. For *sec*-butyltrimethylammonium iodide reduction of reaction temperature to -72° decreased the ratio of *n*-butane to methane by only about 40%. *sec*-Butyltrimethylammonium iodide was not completely soluble in liquid ammonia at the lower reaction temperature.

In Table II are given the ratios of higher alkane to methane from various alkylmethylammonium halides with sodium in liquid ammonia; these ratios are again multiplied by 100 for convenience. In the column on the far right of the table the observed ratio is corrected for unequal numbers of higher alkyl and methyl groups by multiplication by a suitable statistical factor. Similar correction of the ratios in Table II and averaging the results for each *n*-butylmethylammonium halide in Tables II and III gives the following corrected ratios (multiplied as always by 100) with their expected probable limits of error: *n*-Bu₃(CH₃)NBr, 0.66 ± 0.04 ; *n*-Bu₃(CH₃)NI, 0.72 ± 0.02 ; *n*-Bu₂(CH₃)₂NBr, 0.89 ± 0.09 ; *n*-Bu(CH₃)₃NI, 0.90 ± 0.12 ; *n*-Bu(CH₃)₃NCI, 1.01 ± 0.12 ; *n*-Bu(CH₃)₃NBr, 1.18 ± 0.11 . It will be observed that for a given quaternary ammonium cation the ratio is constant within about the expected limits of error as the halide anion is varied. On the whole, however, the ratio increases with increasing number of methyl groups on going from tri-*n*-butylmethylammonium bromide to *n*-butyltrimethylammonium bromide; this increase, though small, appears to be beyond the limits of experimental error. The average value of the ratio is 0.89 with a maximum deviation of ± 0.29 . The data of Table III show that the ratio of higher alkane to methane is, within the probable limits of experimental error, independent of halide anion also for the other ammonium halides tested.

The quaternary ammonium halides of Tables II and III, in summary, give the following average corrected ratios: Et, 0.83 ± 0.06 ; *n*-Bu, 0.89 ± 0.29 ; *n*-Pr, 1.69 ± 0.12 ; *i*-Pr, 13.7 ± 0.8 ; *sec*-Bu, 43.8 ± 2.1 ; Me, $100 < t$ -Bu, $75,000 \pm 18,000$. These ratios are the relative rates of cleavage of groups in liquid ammonia at -33° , methyl being assigned a rate of 100. The corresponding values obtained previously² in dioxane at 102° are: *n*-Pr, 2.4 ± 0.3 ; *n*-Bu, 2.6 ± 0.7 ; Et, 4.2 ± 0.4 ; *i*-Pr, 28.2 ± 1.9 ; *sec*-Bu, 53 ± 3 ; Me, $100 < allyl$, $1050 \pm 120 < t$ -Bu, $10,800 \pm 1000$. While there are some slight alterations of relative reactivity by a factor of about two within each series, the two series of reactivities differ

chiefly only in that the series in liquid ammonia covers a wider range of reactivity (90,000-fold change from ethyl to *t*-butyl) than that in dioxane (4,500-fold change from *n*-propyl to *t*-butyl). A plot (not shown) of the logarithm of the relative rate of cleavage in liquid ammonia *versus* that in dioxane gives a reasonably good straight line. The greater selectivity for cleavage of groups in liquid ammonia than in dioxane must be due in large part to the lower temperature used. The general similarity of the two series suggests that, despite that reaction in dioxane probably takes place with quaternary ammonium cation on the surface of a particle of sodium while reaction in liquid ammonia occurs between quaternary ammonium cation and solvated electrons, the product-determining stages of the two reactions are similar and are governed by similar structural factors.

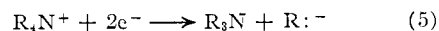
Mechanism of Reductive Cleavage.—Einde's suggestion that the reductive cleavage of quaternary ammonium halides occurs by way of decomposition of the ammonium salt into tertiary amine and alkyl halide has been shown² to be unlikely for tetraalkylammonium halides in dioxane at 102° . Such decomposition appears even less feasible for reductive cleavage in liquid ammonia at -33° .

Jolly⁸ in his study of the reaction between tetraethylammonium bromide and sodium in liquid ammonia obtained triethylamine, hydrogen, ethylene and ethane. He regarded ethane to be formed by way of ethylene which was reduced to ethane by the solution of electrons from sodium in liquid ammonia. While this mechanism could not account for the formation of methane from *N*-methylammonium halides nor for toluene from benzyltrimethylammonium iodide⁶ and while isolated carbon-carbon double bonds are not generally reducible by "chemical agents,"¹⁴ it seemed worthwhile to ascertain whether alkenes were reduced to alkanes under our reaction conditions. No appreciable reduction of butene-1 or of isobutylene was indeed observed under conditions which simulated those used for the reductive cleavages in liquid ammonia. The general constancy of alkane to methane ratios, despite variable yields of olefin, suggests that in other cases as well no appreciable reduction of olefin occurred.

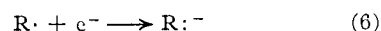
It appears, therefore, that the tetraalkylammonium halides used in the present work reacted *directly* with electrons. These electrons may be those of sodium metal for reactions in dioxane or they may be electrons from the solution of sodium in liquid ammonia. Both types of electrons evidently bring about the same process of reduction. The electron transfer to quaternary ammonium cation may consist of one-electron or two-electron addition in the cleavage step



or



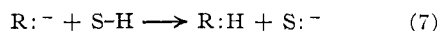
The radicals produced from 4 may be reduced readily to anions



The final products then result from proton transfer

(14) A. J. Birch, *Quart. Rev. (London)*, **4**, 69 (1950).

from the solvent, S-H



These mechanisms should be regarded as leaving unanswered the complex questions as to whether the two-electron addition of equation 5 occurs as two successive one-electron additions or one two-electron addition and whether the cleavages shown in equations 4 and 5 occur during or after the indicated electron additions.

This general scheme of reductive cleavage has been discussed by Birch¹⁴ especially for the cleavage of ethers and alcohols. The influence of structure upon reaction rate (as generally judged by competitive reactions) was, in the cases studied by Birch, such as to suggest that cleavage occurred by two-electron addition. On the other hand, Hazlehurst, Holliday and Pass⁹ have more recently suggested that the cleavage of tetra-*n*-alkylammonium halides was by one-electron addition (equations 4, 6 and 7). Their chief evidence was the formation of traces of ethane from methylammonium halides as discussed previously.

The principal evidence that proton transfer (equation 7) occurs after rather than simultaneously with the formation of carbanions (equations 5 and 6) is that the present cleavages gave similar ratios of products in liquid ammonia and dioxane though dioxane is a poorer proton donor than liquid ammonia. Thus while carbanions having two or more phenyl groups as in 1,1,2-triphenylethylsodium are known to be stable in liquid ammonia and in dioxane, the reaction of 1,1,1-triphenyl-2-chloroethane with sodium in liquid ammonia gave 1,1,1-triphenylethane¹⁵ while with sodium in dioxane 1,1,2-triphenylethylsodium resulted.¹⁶ These reactions were interpreted to indicate that 2,2,2-triphenylethylsodium was protonated rapidly in liquid ammonia but in dioxane existed long enough to undergo rearrangement to the more stable 1,1,2-triphenylethylsodium.

The present work provides information chiefly on the effect of structure upon the cleavage step itself. Interpretation of these data requires knowledge of the effect of structure upon the stability of carbanions and radicals. The order of stability of carbanions in increasing order appears¹⁷ to be *t*-Bu < *sec*-Bu, *i*-Pr < *n*-Bu, *n*-Pr, Et < CH₃. The more stable carbanion is judged to be the more readily formed¹⁸ or the less reactive¹⁹ carbanion. The reasons for the given order of carbanion stability are not agreed upon²⁰ but appear to involve polar

and steric factors. The conclusion seems justified that reactions leading to carbanions have an increasingly higher free energy of activation as hydrogen atoms alpha to the reaction center are replaced successively by alkyl groups.

The order of stability of alkyl free radicals is expected to be the reverse of that given for carbanions, with methyl being the least stable and *t*-butyl the most stable of the simple hydrocarbon radicals which lack multiple bonds. This order of stability is supported by the reactivity of various alkyl halides with sodium vapor²¹ and by the relative rates of abstraction of hydrogen from paraffins by radicals.²² Reactions which give free radicals have a progressively smaller free energy of activation as hydrogen atoms alpha to the reaction center are replaced successively by alkyl groups.

The relative rates of reductive cleavage of alkyl groups from tetraalkylammonium halides by sodium in dioxane or liquid ammonia do not correspond in a simple way to the order expected for either free radical cleavage (eq. 4) or carbanion cleavage (eq. 5). Reductive cleavage also involves the formation of amines as well as hydrocarbons so differences in stability of amines could affect the relative rates of reductive cleavage. The more basic the amine the less readily it might be expected to be formed by reductive cleavage. All the amines formed in the present work, however, have about the same basicity and thus this factor could not account for the large differences observed in the relative rates of cleavage of primary, secondary and tertiary alkyl groups. Some of the small differences such as that noted above for cleavage of *n*-butylmethylammonium halides might be attributed to differences in the basicity of the amines formed.

An important factor affecting reductive cleavage of quaternary ammonium salts should be the relief of steric strain afforded by the cleavage of bulky groups from quaternary nitrogen. The steric strain in ammonium ions and amines can be estimated from the steric strain in homomorphic hydrocarbons.²³ Detailed calculations of steric strain from heats of formation of hydrocarbons in the gas phase at 25° have been made by Spitzer and Pitzer²⁴ and, where appropriate, are summarized in Table IV along with some values calculated in an analogous fashion. According to the table, cleavage of the large alkyl group from alkyltrimethylammonium cations gives products without steric strain while cleavage of the small methyl group may give products (amine in the present case) containing appreciable steric strain. Hence more steric strain is lost, if any, in the cleavage of the larger alkyl group from nitrogen. Cleavage of the large alkyl should in such cases be accelerated relative to cleavage of methyl. While the absolute rate of cleavage of groups from nitrogen must be

(15) J. C. Charlton, I. Dostrovsky and E. D. Hughes, *Nature*, **167**, 986 (1951).

(16) E. Grovenstein, Jr., *THIS JOURNAL*, **79**, 4985 (1957).

(17) A. J. Birch, *Disc. Faraday Soc.*, no. 2, 246 (1947); A. A. Morton, *Chem. Revs.*, **25**, 8 (1944); G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929). Fenton and Ingold (*ibid.*) proposed a mechanism for the cleavage of phosphonium ions by hydroxide ion which bears an interesting similarity to the two-electron addition process given above for cleavage of ammonium ions.

(18) H. Pines and co-workers, *THIS JOURNAL*, **78**, 4316, 5946, 5950 (1956); D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

(19) H. Pines and L. Schaap, *THIS JOURNAL*, **79**, 2956, 4967 (1957); P. D. Partlett, S. Friedman and M. Stiles, *ibid.*, **75**, 1771 (1953); H. Gilman, F. W. Moore and O. Baine, *ibid.*, **63**, 2479 (1941).

(20) H. B. Henbest, *Ann. Rep. on Prog. Chem. (Chem. Soc. London)*, 142 (1956); G. S. Hammond, "Steric Effects in Organic Chemistry," M. S. Newman (ed.), John Wiley and Sons, Inc., New York, N. Y., 1956, p. 439.

(21) E. Warhurst, *Quart. Rev. (London)*, **5**, 44 (1951); A. G. Evans and H. Walker, *Trans. Faraday Soc.*, **40**, 384 (1944); E. T. Butler and M. Polanyi, *ibid.*, **39**, 31 (1943); H. v. Hartel, N. Meer and M. Polanyi, *Z. physik. Chem.*, **19B**, 139 (1932).

(22) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1954, p. 500; F. O. Rice and T. A. Vanderslice, *THIS JOURNAL*, **80**, 291 (1958).

(23) H. C. Brown, *et al.*, *ibid.*, **75**, 1 (1953); **64**, 325 (1942).

(24) R. Spitzer and K. S. Pitzer, *ibid.*, **70**, 1261 (1948).

TABLE IV
 ESTIMATION OF STERIC ACCELERATION FOR REDUCTIVE CLEAVAGE OF QUATERNARY AMMONIUM SALTS

Ammonium salt	(CH ₃) ₃ N ⁺	CH ₃ CH ₂ N ⁺ (CH ₃) ₂	(CH ₃) ₂ CHN ⁺ (CH ₃) ₂	(CH ₃) ₂ CN ⁺ (CH ₃) ₂	(CH ₃) ₃ CCH ₂ N ⁺ (CH ₃) ₂
Homomorph	(CH ₃) ₃ C	CH ₃ CH ₂ C(CH ₃) ₂	(CH ₃) ₂ CHC(CH ₃) ₂	(CH ₃) ₂ CC(CH ₃) ₂	(CH ₃) ₃ CCH ₂ C(CH ₃) ₂
Steric strain in homomorph, kcal./mole	-0.1	+0.2	+2.2	+5.0	+5.2
Steric strain in products from cleavage of larger alkyl group, kcal./mole	0.0	0.0	0.0	0.0	-0.1
Steric strain in products from cleavage of methyl group, kcal./mole	0.0	-0.2	+0.9	+2.2	+2.6
Maximum steric acceleration of higher alkyl to methyl cleavage at 102°	1.00	0.8	3.3	19	37
-33°	1.00	0.7	6.6	100	290

determined in part by the steric strain in the starting quaternary ammonium ion, the relative rate of cleavage of two groups from the same quaternary nitrogen is determined only by the difference in free energy of the two transition states. If it is assumed that the transition state for cleavage has the same steric strain as the products from cleavage and if steric strain affects only the energy of activation and not the entropy of activation, then factors for steric acceleration can be calculated as in the last two lines of Table IV from the differences in activation energy computed by subtraction of the values in the two preceding lines. These factors, which represent how much faster the large alkyl group cleaves than the small methyl because of the relief of steric strain upon reaction, should represent the maximum possible steric acceleration since all the steric strain which is lost upon reaction is assumed to be lost already in the transition state.

These maximum factors for steric acceleration, however, are not large enough by themselves to account for the increase in relative rate of cleavage on going from ethyl (or higher *n*-alkyl) to isopropyl to *t*-butyl. Thus if, as seems reasonable, the over 100-fold slower cleavage in liquid ammonia of ethyl as opposed to methyl is attributed to retardation of cleavage of groups as carbanions by α -alkylation; then if isopropyl is cleaved by a similar mechanism it should cleave still more slowly than ethyl since the 6.7/0.7 fold steric acceleration given in Table IV should not be large enough to offset the large (possibly 50-fold) decrease in rate expected upon further α -methylation. Similarly the 5,500-fold greater rate of cleavage of *t*-butyl over isopropyl cannot alone be due to steric acceleration because Table IV predicts that the maximum steric acceleration possible is 100/6.6 or 15-fold. Since α -alkylation increases radical stability, it is postulated that *t*-butyl and predominantly also isopropyl and *sec*-butyl groups cleave as free radicals under our reaction conditions. Ethyl and higher primary alkyl groups are believed to cleave as carbanions since the 8- to 53-fold increase in rate (or smaller increase after correction for steric acceleration) on going from these primary groups to isopropyl and *sec*-butyl is smaller than would be expected if both primary and secondary groups cleaved as radicals (note that *t*-butyl cleaves 110 or 360 times faster than the secondary alkyl groups even after maximum correction for steric acceleration). In summary, secondary and tertiary alkyl groups cleave from nitrogen by the one-electron transfer process of equation 4, while methyl and higher primary alkyl groups cleave by the two-electron transfer reaction of equation 5.

Bryce-Smith²⁵ has detected primary alkyl radicals in reactions of organoalkali compounds by reaction with cumene to give bicumyl (2,3-diphenyl-2,3-dimethylbutane). The reaction² of *t*-butyltrimethylammonium iodide with sodium in cumene gave 17% yield of isobutane but less than 1.5% of bicumyl. Such a low yield of bicumyl, however, does not necessarily imply that *t*-butyl free radicals were not formed but that they were unreactive toward cumene²⁶ relative to sodium.

While the major factor in determining the relative ease of cleavage of the present alkyl groups from nitrogen is the influence of α -alkylation upon the rate of formation of carbanions or radicals, in other cases steric acceleration may be of major importance. In Table IV are presented calculations for steric acceleration in the cleavage of neopentyltrimethylammonium ion from estimates of the steric strain in homomorphous hydrocarbons.²⁷ These calculations show that the neopentyl group could cleave some 2.6 times faster than methyl if all the steric strain which is lost in the cleavage is lost already in the transition state and if the neopentyl group in absence of steric acceleration cleaves at the same rate as *n*-butyl. While neopentyltrimethylammonium ion does not appear to have been investigated in this regard, cleavage of hexahydro α poconessine methiodide²⁸ by sodium in liquid ammonia occurs 0.41 times as fast as the neopentyl-like cleavage of methyl (after correction for statistical factors) and cleavage of tetrahydroconessimethine dimethiodide²⁸ at the neopentyl-like position occurs at least 14 times faster than cleavage of methyl. Evidently in view of greater branching, tetrahydroconessimethine dimethiodide is more highly strained about one of its ammonium groups than is neopentyltrimethylammonium ion.

Cleavage of Aryltrimethylammonium Ions.—Groenewoud and Robinson²⁹ have studied the cleavage of aryltrimethylammonium chlorides with sodium amalgam in water at steam-bath temperature. From the composition of the amines which were produced, the following relative rates of

(25) D. Bryce-Smith, *J. Chem. Soc.*, 1712 (1955); 1603 (1956).

(26) B. A. Dolgoplosk, B. L. Erusalimskii, V. A. Krol and L. M. Romanov, *Zhur. Obshchei Khim.*, **24**, 1775 (1954); *C. A.*, **49**, 12339 (1955).

(27) H. C. Brown and W. H. Bonner, *This Journal*, **75**, 11 (1953).

(28) R. D. Haworth, L. H. C. Lunts and J. McKenna, *J. Chem. Soc.*, 3749 (1956). Dr. J. McKenna, in a personal communication, has kindly pointed out that these cleavages were run under preparative conditions and that the differences in the results from tetrahydroconessimethine dimethiodide and hexahydro α poconessine methiodide may be related to the much lower solubility of the latter in liquid ammonia.

(29) P. Groenewoud and R. Robinson, *J. Chem. Soc.*, 1032 (1934).

cleavage of groups may be calculated, methyl being assigned a rate of 100 and the rates being corrected statistically for unequal numbers of groups: *p*-anisyl, 76 < *p*-tolyl, 130 < *m*-tolyl, 450 < *o*-tolyl, 510; *m*-anisyl, 530 < phenyl, 740 < *p*-biphenyl, 1800 < *o*-anisyl, 2300 < *m*-biphenyl, 3700 < β -naphthyl, 5400. Groenewoud and Robinson noted that it was "extremely difficult to generalize on the basis of these results, which evidently represent the combined operation of several factors." In light of the present work and related work on cleavages of ethers¹⁴ it now appears possible to discuss the several factors involved.

A primary factor is that these cleavages occur with formation of carbanions in the initial cleavage step (but see below). The justification for this mechanistic assignment is that phenyl cleaves faster than methyl as expected for carbanions, and that methyl doubtless cleaves as a carbanion as discussed previously. For cleavage as a radical phenyl would be expected to cleave at about the same slow rate as for cleavage of methyl as a radical.²¹ Methyl cleavage from aryltrimethylammonium ion doubtless receives some acceleration relative to aryl because methyl cleavage gives rise to a dimethylaniline while aryl cleavage gives the more basic trimethylamine (see previous discussion). Moreover the effect of *meta* and *para* substituents on the rate of cleavage of phenyl is about what would be predicted for cleavage as a carbanion, *i.e.*, electron-donor groups retard and electron-withdrawing groups accelerate the cleavage. A similar effect of substituents has been observed in the cleavage of diphenyl ethers³⁰ by sodium in liquid ammonia. Both in the cleavage of ethers and ammonium salts, the *o*-methyl group is less deactivating and the *o*-methoxyl group is possibly more activating than might have been expected from usual polar effects. Whether these reactivities are due to steric effects,²³ an unusual type of resonance¹⁴ or other causes is unclear.

In solvents such as water, which have labile protons, it seems doubtful that carbanions are formed as actual intermediates. Instead reactions 5 and 7 above probably occur simultaneously such that proton binding to the carbanion occurs partially in the transition state. Under these circumstances we should speak of the cleavage as occurring by way of transition states possessing carbanion-like character rather than by way of carbanions. The simplified arguments above are otherwise unaffected except for the complication that different degrees of binding of the proton in the transition state are conceivable.

Cleavage of Alkyl Groups from Ethers.—In the cleavage of *o*-alkoxyanisoles by sodium in liquid

(30) F. J. Sowa, *et al.*, *THIS JOURNAL*, **59**, 603, 1488 (1937); **60**, 94 (1938).

ammonia, Birch³¹ found that benzyl and carboxymethyl cleave in preference to methyl while methyl cleaves in preference to *n*-propyl, *n*-amyl or isopropyl. These results can be rationalized on the basis of cleavage of groups as carbanions.¹⁴ In light of the present work on ammonium halides it seemed of interest to see whether reductive cleavage of ethers by way of radicals could be effected. For this purpose *t*-butyl methyl ether was studied. This ether cleaved² to the extent of 0.04% or less with sodium or potassium in dioxane at reflux, with sodium in cumene at 102° or with potassium in boiling tetrahydrofuran. In the present work with sodium in liquid ammonia at -33°, a large excess of *t*-butyl methyl ether was cleaved to the extent of 0.8% based on sodium or 0.05% based on ether. The gaseous cleavage product was isobutane in so far as could be determined. The slow cleavage of *t*-butyl methyl ether is striking since in competitive cleavages of quaternary ammonium ions in dioxane, the *t*-butyl group cleaved, relative to methyl, ten times more readily than allyl.² Furthermore allyl ether³² and allyl alcohols¹⁴ are known to undergo cleavage by alkali metals under similar conditions. A partial explanation is that cleavage of *t*-butyl, but not allyl, is aided by steric acceleration when the *t*-butyl group is on quaternary nitrogen but not, in the present case, when on oxygen. According to Table IV the cleavage of *t*-butyl as opposed to methyl from *t*-butyltrimethylammonium is aided, at most, some 20-fold by relief of steric strain at 102°, while no appreciable steric acceleration is expected for cleavage of allyltrimethylammonium ion. On the other hand, neither the cleavage of *t*-butyl methyl ether (the homomorph of 2,2-dimethylbutane) nor diallyl ether should show appreciable steric acceleration. Even allowing for steric acceleration, however, *t*-butyl methyl ether would be expected to cleave at least half as readily as diallyl ether, especially since methoxide anion might be formed more readily than allyl oxide as judged by the relative acidities³³ of the corresponding alcohols. It may be that, in accord with their lower reactivity, ethers display more selectivity in reductive cleavage of groups than do quaternary ammonium ions. Further study of reductive cleavage of ethers would appear valuable.

Acknowledgments.—The authors wish to acknowledge support of this research by Frederick Gardner Cottrell Grants from the Research Corporation and a fellowship supplied by the Rayonier Corporation.

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(31) A. J. Birch, *J. Chem. Soc.*, 102 (1947).

(32) A. A. Morton, E. E. Magat and R. L. Letsinger, *THIS JOURNAL*, **69**, 950 (1947); R. L. Letsinger and J. G. Traynham, *ibid.*, **70**, 3342 (1948).

(33) J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952).